Laser-Induced Graphene-Based Materials for Electrochemical Energy Storage and Conversion

by

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ABSTRACT

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The ever-increasing demand for clean energy has led to extensive research on the development of renewable energy technologies for energy storage and conversion, such as electrochemical capacitors, lithium-ion batteries, fuel cells, photo/electrical water splitting, and rechargeable metal-O_2_ batteries. This thesis focused on the development of laser-induced graphene (LIG) derived materials and devices for electrochemical energy storage and conversion. LIG is a 3D porous graphene material fused to a flexible substrate that is prepared by a one-step laser scribing process on commercial polyimide (PI) film. The LIG derived from PI is highly porous and is easily synthesized under ambient conditions in a scalable process. This thesis covers the design, synthesis, characterization and mechanistic study of LIG derived devices and catalysts in 5 chapters:

Chapter 1 discusses the study on the all-solid-state, flexible, symmetric, and asymmetric LIG microsupercapacitors which are fabricated by a simple method in a scalable fashion from LIG on commercial polyimide films, followed by the electrodeposition of active materials on the interdigitated in-plane architectures. These microsupercapacitors demonstrate comparable energy density to commercial
lithium thin-film batteries, yet exhibit more than two orders of magnitude higher power density with good mechanical flexibility.

Chapter 2 describes the LIG-based electrodes with good activity for full water splitting and presents a water electrolyzer where H₂ and O₂ are simultaneously generated on either side of the plastic sheet and can thereby be selectively captured. In the rechargeable metal-O₂ batteries, the cathode reactions (OER/ORR) often show significantly sluggish kinetics such as high overpotential and high Tafel slope. Therefore, I also focused on the LIG derived catalysts for the oxygen electrocatalysis.

In Chapter 3, the oxidation of LIG by O₂ plasma to form oxidized LIG boosts its performance in both OER and ORR, resulting in an enhanced activity towards rechargeable Li-O₂ battery.

In Chapter 4, I worked with collaborators and developed a distinctive method to prepare metal oxide/LIG composites as efficient catalysts for water oxidation (OER). Unlike the conventional methods, such as solvo-/hydro-thermal, thermal pyrolysis or chemical vapor deposition processes, my method synthesizes the NiFe-based catalysts through a facile laser scribing process without any tedious procedures.

The LIG method is further developed to prepare bifunctional catalysts for metal-O₂ batteries as shown in Chapter 5. The catalysts exhibited high activity in both Li-O₂ and Zn-air batteries. It is worth noting that this method is newly developed, and its application is still expanding. We would anticipate that the method could be
applied for the synthesis of a variety of metal-based catalysts for different reactions, and the dimension of metal species would be ranging from nanoparticles to sub-nano scale such as atomically dispersed supported metal catalysts, and even to metal-free heteroatom-doped LIG, with properly selected precursors and procedures.
Acknowledgments

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<tbody>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller measurement</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>DI water</td>
<td>deionized water</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>EASA</td>
<td>electrochemically active surface area</td>
</tr>
<tr>
<td>EDLC</td>
<td>electric double layer capacitance</td>
</tr>
<tr>
<td>EIS</td>
<td>electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>GO</td>
<td>graphene oxide</td>
</tr>
<tr>
<td>HER</td>
<td>hydrogen evolution reaction</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>inductively coupled plasma optical emission spectrometry</td>
</tr>
<tr>
<td>LSV</td>
<td>linear sweep voltammetry</td>
</tr>
<tr>
<td>MSC</td>
<td>microsupercapacitors</td>
</tr>
<tr>
<td>ORR</td>
<td>oxygen reduction reaction</td>
</tr>
<tr>
<td>OER</td>
<td>oxygen evolution reaction</td>
</tr>
<tr>
<td>PANI</td>
<td>polyaniline</td>
</tr>
<tr>
<td>PI</td>
<td>polyimide</td>
</tr>
<tr>
<td>PVA</td>
<td>poly(vinyl alcohol)</td>
</tr>
<tr>
<td>RHE</td>
<td>reversible hydrogen electrode</td>
</tr>
<tr>
<td>RDE</td>
<td>rotating-disk electrode</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>RDS</td>
<td>rate-determining step</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
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<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TOF</td>
<td>turnover frequency</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<td>X-ray diffraction</td>
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High-Performance Pseudocapacitive Microsupercapacitors from Laser-Induced Graphene

This chapter was entirely copied from reference. 

1.1. Introduction

The development and miniaturization of energy storage devices are facilitating the growth of modern micro-electronic systems. Microbatteries are presently the major power source for miniaturized electronic devices even though they suffer from sluggish charge/discharge processes and a limited cycle life. Microsupercapacitors (MSCs), on the other hand, have high power density, fast charge/discharge rates, and long service life. And with their in-plane interdigitated electrodes, they show a pathway to replace microbatteries. However, developing
easily fabricated MSCs with high energy densities, close to or exceeding those in microbatteries, without sacrificing other electrochemical characteristics, is a crucial challenge. The most common strategy is to use photolithography to prepare interdigitated patterns of highly conductive carbon materials to provide the electrochemical double layer capacitance (EDLC). Recently, laser writing technology has also been used to reduce and pattern graphene oxide (GO) as interdigitated electrodes in MSCs. However, the synthesis and post-reaction treatment of GO and the problematic stability of the remaining GO in such devices presents commercialization challenges. Since the energy density of the device is determined by its capacitance and working voltage \((E = CV^2/2)\), further improvement of its energy storage relies on enhancing either of these parameters. To increase device capacitance, pseudocapacitive materials, such as transition metal oxides and electrically conductive polymers, are loaded onto the electrodes to provide pseudocapacitance from surface redox reactions. However, this fabrication strategy is limited by either high-cost patterning processes or harsh synthetic conditions, slowing deployment in commodity electronic devices. Alternatively, organic electrolytes are used for their higher working voltage, resulting in further improvement in energy storage. However, safety issues, complex fabrication processes and strict conditions for the use of organic electrolytes, has limited their widespread application. An alternative approach is to make asymmetric MSCs without using an organic electrolyte.
Recently, our group developed a simple and scalable method to prepare patterned porous graphene on a polyimide (PI) substrate by laser-writing patterns in air, and the resulting laser induced graphene (LIG) showed its promising applications in miniaturized energy storage devices.\textsuperscript{28-30} Here, we combine the laser induction process with subsequent electrodeposition of pseudocapacitive materials for the fabrication of all-solid-state, flexible symmetric and asymmetric MSC devices that show greatly improved electrochemical performance. A CO\textsubscript{2} laser is first used to convert the PI into porous LIG with an interdigitated architecture, which works not only as EDLC electrodes, but also as a flexible and conductive matrix for the electrodeposition of pseudocapacitive materials. Two types of pseudocapacitive materials, manganese dioxide (MnO\textsubscript{2}) or ferric oxyhydroxide (FeOOH), and polyaniline (PANI), representing characteristic transition metal oxides and conductive polymers, are electrodeposited onto the LIG forming LIG-MnO\textsubscript{2}, LIG-FeOOH, and LIG-PANI composites. They are then assembled into all-solid-state flexible symmetric LIG-MnO\textsubscript{2}-MSCs and LIG-PANI-MSCs, and asymmetric MSCs using LIG-FeOOH as a negative electrode and LIG-MnO\textsubscript{2} as a positive electrode (LIG-FeOOH//LIG-MnO\textsubscript{2}) that are free of current collectors, binders, and separators due to the well-defined patterns that avoid short circuiting the electrodes. All these devices demonstrate comparable energy densities to microbatteries without sacrificing their good rate performance, cycling stability, and mechanical flexibility.
1.2. High-Performance Pseudocapacitive Microsupercapacitors from Laser-Induced Graphene

1.2.1. Device Fabrication and Characterization.

Figure 1.1. The dimension of the MSCs with the interdigitated electrodes in plane. The device area ($A_{Device}$) refers to the total surface area of interdigitated electrodes and the space between them. It is equal to electrode width ($W$) multiplied by the length ($L$): $A_{Device} = W \times L = 0.41 \text{ cm} \times 1.85 \text{ cm} = 0.75 \text{ cm}^2$. The device volume ($V_{Device}$) is estimated as: $V_{Device} = W \times L \times H$, where $H$ stands for the height of the hybrid material and can be measured from previous cross-sectional SEM images.

**Synthesis and fabrication of LIG.** The synthesis and patterning of LIG from a polyimide sheet was done as we described previously. Kapton® polyimide films (McMaster-Carr, Cat. No. 2271K3, thickness: 0.005") were used as received. LIG was generated using a CO$_2$ laser cutter system (Universal X-660 laser cutter platform) on Kapton® polyimide film at a power of 4.8 W. All samples were prepared under room temperature and ambient air. LIG was patterned into 12 interdigitated electrodes with a length of 4.1 mm, a width of 1 mm, and a spacing of $\sim$300 µm between two
neighboring microelectrodes (Figure 1.1). After that, Pellco® colloidal silver paint (No. 16034, Ted Pella) was first applied on the common areas of both electrodes for better electrical contact. The electrodes were then extended with conductive copper tape which were connected to an electrochemical workstation for testing. A Kapton® polyimide tape was employed followed by an epoxy (Machineable-fast set, Reorder # 04002, Hardman®) sealing to protect the common areas of the electrodes from electrolyte.

**Synthesis of LIG-MnO$_2$** Electrodeposition of MnO$_2$ on LIG was achieved with a three-electrode setup. LIG on a PI sheet served as the working electrode, which was immersed into an aqueous solution containing 0.01M Mn(CH$_3$COO)$_2$ at ~60 °C. Platinum foil (Sigma-Aldrich) was the counter electrode and Ag/AgCl (Fisher Scientific) was the reference electrode. A constant current density of 1 mA cm$^{-2}$ was applied for a designated time to ensure good deposition of MnO$_2$ on the sample. The amount of MnO$_2$ onto LIG was controlled by adjusting the deposition time. After electrodeposition, the sample was withdrawn and washed with deionized water to remove excess electrolyte, and then placed in a vacuum desiccator overnight (~120 mm Hg).

**Synthesis of LIG-FeOOH.** Electrodeposition of FeOOH on LIG was achieved with a two-electrode setup. LIG on a PI sheet served as the working electrode, which was immersed into an aqueous solution containing 0.1 M FeCl$_3$. The pH of FeCl$_3$ solution was 2, adjusted by 1.0 M HCl. A constant current density of 15 mA cm$^{-2}$ was applied for a designated time to ensure sufficient deposition of FeOOH on the sample.
The amount of FeOOH onto LIG was controlled by adjusting the deposition time. After electrodeposition, the sample was withdrawn and washed with deionized water to remove excess electrolyte, and then placed in a vacuum desiccator overnight (~120 mm Hg).

**Synthesis of LIG-PANI.** Electrodeposition of PANI on LIG was achieved with a three-electrode setup. LIG on a PI sheet served as the working electrode, which was immersed into an aqueous solution containing 0.1 M aniline and 1.0 M H₂SO₄. With a platinum counter electrode and Hg/Hg₂Cl₂ (Fisher Scientific) reference electrode, PANI was electrochemically deposited onto LIG by cycling within the potential window from -0.20 V to 0.95 V vs. Hg/Hg₂Cl₂. The amount of PANI onto LIG was controlled by the cycle number of deposition. After electrodeposition, LIG-PANI was treated with 1.0 M H₂SO₄ for 1 h. A uniform dark green film was obtained after washing with deionized water to remove excess electrolyte and drying in a vacuum desiccator overnight (~120 mm Hg).

**Fabrication of the flexible all-solid-state MSCs.** Polymeric gel electrolytes of PVA/LiCl and PVA/H₂SO₄ were prepared according to the previously reported method¹⁷ and used in LIG-MnO₂ and LIG-FeOOH//LIG-MnO₂, and LIG-PANI, respectively. For PVA/LiCl, it was made by stirring 10 mL of DI water, 2.0 g of LiCl (Sigma-Aldrich), and 1.0 g of PVA (M₆ = 50000, Aldrich No. 34158-4) at 80 °C overnight. For PVA/H₂SO₄, it was made by stirring 10 mL of DI water, 1.0 mL of sulfuric acid (98%, Sigma-Aldrich), and 1.0 g of PVA at 80 °C overnight. ~ 0.25 mL of the electrolyte was applied to the active area of the devices and was dried under
ambient conditions for 4 h. The all-solid-state MSCs were obtained after drying in a vacuum desiccator (~120 mm Hg) overnight for further solidification of the electrolyte.

**Device Characterization.** The electrochemical performances of the flexible all-solid-state MSCs were characterized by CV, galvanostatic charge-discharge experiments, and EIS using an electrochemical station (CHI 608D). The areal specific capacitance ($C_A$) and volumetric specific capacitance ($C_V$) of electrode materials were calculated from galvanostatic charge-discharge curves according to **Equation 1.1**, respectively:

$$C_A = \frac{4 \times I}{A_{Device} \times (dV/dt)}$$

$$C_A = \frac{4 \times I}{V_{Device} \times (dV/dt)}$$

**Equation 1.1. Calculation of the capacitance of the electrode materials.**

where $I$ is the current applied, $A_{Device}$ is the total area of the device (**Figure 1.1**), $V_{Device}$ is the total volume of the device (**Figure 1.1**), and $dV/dt$ is the slope of the discharge curve.

The areal capacitance ($C_{Device,A}$) and volumetric capacitance ($C_{Device,V}$) of the MSCs were calculated by using **Equation 1.2**, respectively:

$$C_{Device,A} = C_A / 4$$
\[ C_{\text{Device,V}} = \frac{C_V}{4} \]

**Equation 1.2. Calculation of the capacitance of the devices.**

The areal energy density \( (E_{\text{Device,A}}) \) and volumetric energy density \( (E_{\text{Device,V}}) \) of the MSCs were calculated by using **Equation 1.3**, respectively:

\[
E_{\text{Device,A}} = \frac{C_{\text{Device,A}} \times V^2}{2 \times 3600}
\]

\[
E_{\text{Device,V}} = \frac{C_{\text{Device,V}} \times V^2}{2 \times 3600}
\]

**Equation 1.3. Calculation of the energy density of the devices.**

where \( V \) is the applied voltage.

The areal power density \( (P_{\text{Device,A}}) \) and volumetric power density \( (P_{\text{Device,V}}) \) of the MSCs were calculated by using **Equation 1.4**, respectively:

\[
P_{\text{Device,A}} = \frac{E_{\text{Device,A}} \times 3600}{t}
\]

\[
P_{\text{Device,V}} = \frac{E_{\text{Device,V}} \times 3600}{t}
\]

**Equation 1.4. Calculation of the power density of the devices.**

where \( t \) is the discharge time.
1.2.2. Result and Discussion

Figure 1.2. Fabrication and the structural morphology of the LIG-MnO$_2$-MSC. (a) Scheme of the fabrication of MSCs with LIG-MnO$_2$, which is similar to the formation of LIG-FeOOH, or LIG-PANI. 1, 2, 3, and 4 are epoxy adhesive, silver paste, Kapton tape and copper tape, respectively. (b) Digital photograph of one MSC device. (c) Cross-sectional SEM images of LIG-MnO$_2$. Scale bar is 100 µm. (d-g) SEM images of top view of (d, e) LIG, and (f, g) MnO$_2$ in LIG-MnO$_2$. Scale bars are 100 µm for d, f and 2 µm for e, g. The lined-pattern in d and f is due to raster scanning of the laser.
The two-step syntheses of the hybrid materials, LIG-MnO$_2$, LIG-FeOOH, and LIG-PANI, and the fabrication into MSCs are shown in Figure 1.2a. CO$_2$ laser induction of the PI substrate was first conducted to form patterned LIG with 12 in-plane interdigitated electrodes (6 per polarity), onto which the pseudocapacitive materials, MnO$_2$, FeOOH, or electrically conductive PANI, were electrodeposited to form the composites of LIG-MnO$_2$, LIG-FeOOH, or LIG-PANI. The amount of MnO$_2$, FeOOH, or PANI in the composites was easily controlled by adjusting the deposition time or cycles, and here labeled as LIG-MnO$_2$-X and LIG-FeOOH-X, (where X represents the deposition time), and LIG-PANI-Y (where Y represents the number of deposition cycles). Details for LIG synthesis and electrodeposition of MnO$_2$, FeOOH, or PANI can be found in the experimental section. Solid-state polymer electrolyte containing poly(vinyl alcohol) (PVA) was used to complete the fabrication of the MSC devices. MSCs of various sizes can be prepared on demand by computer-controlled patterning in air at room temperature during the laser induction process (Figure 1.3). Figure 1b shows a digital photograph of one fully fabricated MSC device using this method. Figure 1.2c shows the cross-sectional scanning electron microscopy (SEM) images of LIG-MnO$_2$-2.5h, in which MnO$_2$ was observed to deposit into the LIG layer. The average thickness of the composite depends on the electrodeposition time or cycles and increases from 34 µm of LIG alone to 101 µm of LIG-MnO$_2$-4.0h, 76 µm of LIG-PANI-15, and 41 µm of LIG-FeOOH-1.5h (Figure 1.4, Figure 1.5, Figure 1.6 and Figure 1.7). Figure 1.2d-g show the top view SEM images of LIG and MnO$_2$, respectively. While LIG forms a porous thin film structure that could work as a
conductive matrix for the subsequent electrodepositions, the deposited MnO$_2$ forms a flower shape. The cross-sectional and top view SEM images of LIG-FeOOH and LIG-PANI are also provided in Figure 1.7. The morphologies of LIG-MnO$_2$, LIG-FeOOH, and LIG-PANI are further characterized by transmission electron microscopy (TEM) as shown in Figure 1.8, Figure 1.9 and Figure 1.10. Crystallized MnO$_2$, FeOOH, and nanofibril PANI were found to directly deposit onto the LIG. Raman spectroscopy, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) were also used to study the composite compositions (Figure 1.11).$^{28,31}$

![Image](image_url)

**Figure 1.3.** Digital image of LIG on PI sheet with different sizes. The unit of the ruler in the image is centimeters.
Figure 1.4. Cross-sectional SEM images of LIG taken at different locations in the same sample. All of them exhibit a height of ~34 µm. The scale bars are 100 µm.
Figure 1.5. Cross-sectional SEM images of LIG-MnO₂.
(a-c) LIG-MnO₂-1.0h, (d-f) LIG-MnO₂-1.5h, (g-i) LIG-MnO₂-2.0h, (j-l) LIG-MnO₂-2.5h, (m-o) LIG-MnO₂-3.0h, and (p-r) LIG-MnO₂-4.0h, indicating the height of these samples are ~ 76 µm, ~ 76 µm, ~ 83 µm, ~ 89 µm, ~ 96 µm, and ~ 101 µm, respectively. In images (p-r), there is a ~ 25 µm vacancy between the upper and bottom layer due to sample preparation, so the actual sample height is calculated as 101 µm. The scale bars are 100 µm.
Figure 1.6. Cross-sectional SEM images of LIG-PANI. (a-c) LIG-PANI-5, (d-f) LIG-PANI-10, and (g-i) LIG-PANI-15, indicating the height of the samples are ~49 µm, ~61 µm, and ~76 µm, respectively. The scale bars are 100 µm.

Figure 1.7. Cross-sectional and top SEM images of LIG-FeOOH and LIG-PANI. (a) Cross-sectional SEM image of LIG-FeOOH-1.5h, indicating the height of ~41 µm. (b, c) Top view SEM images of FeOOH in LIG-FeOOH at different resolutions. (d) Cross-sectional SEM image of LIG-PANI. (e, f) Top view SEM images of PANI
in LIG-PANI at different resolutions. The scale bars are 100 µm for a, b, d, and e and 2 µm for c and f. The lined-pattern in b and e is due to the raster scanning of the laser.

Figure 1.8. TEM images of the LIG-MnO$_2$.
(a) The TEM image of the LIG-MnO$_2$ hybrid material. (b-d) The TEM images of MnO$_2$ in LIG-MnO$_2$ at different resolutions. The scale bar is 400 nm for a, 20 nm for b, c, and 10 nm for d.
Figure 1.9. TEM images of the LIG-FeOOH.
(a) The TEM image of the LIG-FeOOH hybrid material. (b, c) The TEM images of FeOOH in LIG-FeOOH at different resolutions. The scale bar is 200 nm for a and 10 nm for b,c.

Figure 1.10. TEM images of the LIG-PANI hybrid material.
(a) The TEM image of the LIG-PANI hybrid material. The scale bar is 4 μm. (b) The TEM image of PANI. The scale bar is 200 nm. (c) HRTEM image of LIG with graphitic edges. The scale bar is 10 nm. (d) HRTEM image of PANI with amorphous character. The scale bar is 10 nm.
Figure 1.11. Raman, XRD and XPS characterization of the MSCs. (a) Raman spectra of LIG and LIG-PANI-15, (b) XRD patterns of LIG, LIG-PANI-15, LIG-MnO$_2$-2.5h, and LIG-FeOOH-1.5h, (c) XPS spectra of LIG, LIG-PANI-15, LIG-MnO$_2$-2.5h, and LIG-FeOOH-1.5h, (d) Elemental XPS spectrum of Mn 2p for LIG-MnO$_2$-2.5h, (ed) Elemental XPS spectrum of Fe 2p for LIG-FeOOH-1.5h. C1s peak (284.5 eV) was used as a standard to correct the data.

Figure 1.11a shows the Raman spectra of LIG and LIG-PANI-15. The characteristic peaks at $\sim$ 1350 cm$^{-1}$, $\sim$ 1597 cm$^{-1}$ and $\sim$ 2707 cm$^{-1}$ from LIG sample represent the D band, G band and 2D bands, respectively, indicating the graphitic structure of LIG.\textsuperscript{28} The polyaniline peaks from 1000 cm$^{-1}$ to 1600 cm$^{-1}$ in LIG-PANI-15 sample confirm the formation of PANI.\textsuperscript{32} Figure 1.11b shows the XRD patterns of LIG, LIG-PANI-15, LIG-MnO$_2$-2.5h, and LIG-FeOOH-1.5h. LIG showed a strong diffraction peak (002) of graphite at 26°.\textsuperscript{28} LIG-PANI-15 shows two peaks centered at 15.3° and 26°, resulting from the periodicity both perpendicular and parallel to the polymer
chain, respectively.\textsuperscript{32} The XRD pattern of LIG-MnO\textsubscript{2}-2.5h can be indexed to $\alpha$-MnO\textsubscript{2}.\textsuperscript{31} Due to the relatively small size of the crystals, the XRD pattern peaks of MnO\textsubscript{2} in LIG-MnO\textsubscript{2}-2.5h become broad and weak. The XRD peak of LIG in LIG-MnO\textsubscript{2}-2.5h is covered by MnO\textsubscript{2}. The XRD pattern of LIG-FeOOH-1.5h can be indexed to $\gamma$-FeOOH.\textsuperscript{33} Figure 1.11c shows XPS spectra of LIG, LIG-PANI-15, LIG-MnO\textsubscript{2}-2.5h and LIG-FeOOH-1.5h. LIG-PANI-15 contained four elements, C, N, O, and trace S from the sulfuric acid. LIG-MnO\textsubscript{2}-2.5h contained three main elements, C, O, and Mn. LIG-FeOOH-1.5h contained four elements, Fe, O, C, and Cl from FeCl\textsubscript{3}. The oxidation state of Mn in LIG-MnO\textsubscript{2}-2.5h is further confirmed by high-resolution XPS as shown in Figure 1.11d. The spin energy separation of Mn $2p_{3/2}$ and Mn $2p_{1/2}$ centered at 642.5 eV and 654.2 eV is 11.7 eV, which is in good agreement with reported data of Mn $2p_{3/2}$ and Mn $2p_{1/2}$ in MnO\textsubscript{2}.\textsuperscript{34} The oxidation state of Fe in LIG-FeOOH-1.5h is also studied by high-resolution XPS as shown in Figure 1.11e, confirming Fe existing in FeOOH.\textsuperscript{33}
Figure 1.12. Electrochemical performance of LIG-MnO$_2$ and LIG-PANI MSCs. (a) CV curves of LIG-MnO$_2$-X and LIG at a scan rate of 5 mV s$^{-1}$. (b) Galvanostatic charge discharge curves of LIG-MnO$_2$-X and LIG at a current density of 0.5 mA cm$^{-2}$. (c) Areal specific capacitance of LIG-MnO$_2$-X and LIG over a current density range of 0.5 and 8.0 mA cm$^{-2}$. (d) CV curves of LIG-PANI-Y and LIG at a scan rate of 10 mV s$^{-1}$. (e) Galvanostatic charge discharge curves of LIG-PANI-Y and LIG at a current density of 0.5 mA cm$^{-2}$. (f) Areal specific capacitance of LIG-PANI-Y and LIG over a current density range of 0.5 and 20.0 mA cm$^{-2}$. (g) Cycling stability of LIG-MnO$_2$-2.5h at the current density of 1.0 mA cm$^{-2}$. (h) Cycling stability of LIG-PANI-15 at the current density of 0.8 mA cm$^{-2}$.

We first studied the electrochemical performance of LIG-MnO$_2$-MSCs with LiCl/PVA as the electrolyte using cyclic voltammetry (CV) and galvanostatic charge-discharge experiments in a potential window from 0 to 1.0 V. Figure 1.12a shows the
CV curves of LIG-MnO$_2$-X and LIG at a scan rate of 5 mV s$^{-1}$. Although LIG is known to contribute capacitance by the EDLC mechanism,$^{28}$ the CV curve of LIG is minuscule compared to those of LIG-MnO$_2$-X, demonstrating that most of the capacitance comes from the pseudocapacitance of MnO$_2$. Also, aside from the much larger CV curve area, the pseudo-rectangular CV shape of LIG-MnO$_2$-X indicates good capacitive behavior.$^5$

**Figure 1.13** shows CV curves of LIG-MnO$_2$-X at a scan rate ranging from 2 to 100 mV s$^{-1}$, demonstrating a proportional current increase with an increasing scan rate. The distorted CV shapes of the samples with more MnO$_2$ content at high scan rates may result from the decreased electrical conductivity. **Figure 1.12b** shows the galvanostatic charge-discharge curves of LIG-MnO$_2$-X at a current density of 0.5 mA cm$^{-2}$. The curve from LIG alone is nearly negligible, again demonstrating little contribution in capacitance from LIG in the composite of LIG-MnO$_2$, which is consistent with the CV analysis.$^5$ **Figure 1.14** further shows the galvanostatic charge-discharge curves of these samples at varying current densities. The nearly symmetrical charging and discharging curves and small voltage drops at initial discharge states indicate good capacitive behavior and high conductivity within the electrodes.$^{35}$ Based on the galvanostatic charge-discharge curves, the areal and volumetric specific electrode capacitance of LIG-MnO$_2$-X are calculated and plotted in **Figure 1.12c** and **Figure 1.15**. Here, the total area of each MSC device ($A_{\text{Device}}$) includes the interdigitated electrodes and the spaces between them, and the volume is equal to $A_{\text{Device}}$ multiplied by the height of the composite (**Figure 1.1**). More MnO$_2$ content in the LIG-MnO$_2$ composite results in a higher capacitance at low current.
density, as evidenced by the highest areal and volumetric specific capacitances of 934 mF cm\(^{-2}\) and 93.4 F cm\(^{-3}\), respectively, from LIG-MnO\(_2\)-4.0h at a current density of 0.5 mA cm\(^{-2}\). At the same current density, the areal and volumetric specific capacitance of LIG alone is less than 0.8 mF cm\(^{-2}\) and 0.2 F cm\(^{-3}\), indicating that most of the capacitance is coming from the pseudocapacitance of MnO\(_2\) in the LIG-MnO\(_2\) composite. With increasing current density, the capacitance from the sample with less MnO\(_2\) decreases more slowly. At a high current density of 8.0 mA cm\(^{-2}\), the specific capacitance of LIG-MnO\(_2\)-2.5h is maximized, with an areal value of 281 mF cm\(^{-2}\) and a volumetric value of 31.5 F cm\(^{-3}\), most likely due to the relatively higher conductivity of the LIG-MnO\(_2\) composite when less MnO\(_2\) was deposited.
Figure 1.13. Cyclic voltammetry curves of LIG-MnO$_2$. (a) LIG-MnO$_2$-4.0h, (b) LIG-MnO$_2$-3.0h, (c) LIG-MnO$_2$-2.5h, (d) LIG-MnO$_2$-2.0h, (e) LIG-MnO$_2$-1.5h, (f) LIG-MnO$_2$-1.0h, and (g) LIG over a scan rate range of 2 and 100 mV s$^{-1}$ in the potential window from 0 to 1.0 V.
Figure 1.14. Galvanostatic charge discharge curves of LIG-MnO$_2$. (a) LIG-MnO$_2$-4.0h, (b) LIG-MnO$_2$-3.0h, (c) LIG-MnO$_2$-2.5h, (D) LIG-MnO$_2$-2.0h, (E) LIG-MnO$_2$-1.5h, (F) LIG-MnO$_2$-1.0h, and (G) LIG over a current density range of 0.5 to 8.0 mA cm$^{-2}$ in the potential window from 0 to 1.0 V.
LIG-PANI-MSCs using H₂SO₄/PVA as the electrolyte were also studied from CV and galvanostatic charge discharge experiments in a potential window from 0 to 0.8 V (Figure 1.12d, e, Figure 1.16 and Figure 1.17). Figure 1.12f and Figure 1.18 show the calculated areal and volumetric specific electrode capacitance of LIG-PANI-Y. LIG-PANI-15 has the best performance among all the samples with an areal and volumetric specific capacitance of 361 mF cm⁻² and 47.5 F cm⁻³, respectively, at a current density of 0.5 mA cm⁻². In comparison, LIG itself is only 8.4 mF cm⁻² and 1.8 F cm⁻³ at the same current density. When the current density increases to 20 mA cm⁻², the specific capacitance of LIG-PANI-15 still remains at 271 mF cm⁻² and 35.6 F cm⁻³ with a high capacitance retention of 75 %, indicating the good rate performance of LIG-PANI-15. The cyclability of the fabricated devices from LIG-MnO₂ and LIG-PANI
were also tested. After 6000 cycles of charge-discharging test, the capacitance of LIG-MnO$_2$-2.5h and LIG-PANI-15 remained over 82 % and 97 %, respectively, showing excellent stability of the devices based on these hybrid composites (Figure 1.12g, h).

**Figure 1.16.** Cyclic voltammetry curves of LIG-PANI.
(a) LIG-PANI-15, (b) LIG-PANI-10, (c) LIG-PANI-5, and (d) LIG over a scan rate range of 2 and 100 mV s$^{-1}$ in the potential window from 0 to 0.8 V.
Figure 1.17. Galvanostatic charge discharge curves of LIG-PANI. (a,b) LIG-PANI-15, (c,d) LIG-PANI-10, (e,f) LIG-PANI-5, (g,h) LIG over a current density range of 0.5 to 20.0 mA cm\(^{-2}\) in the potential window from 0 to 0.8 V.
To meet the specific energy and power needs for practical applications, multiple MSCs from LIG-MnO$_2$ or LIG-PANI can also be scaled up and assembled in either series or parallel configurations (Figure 1.19). Compared with a single MSC, the discharge time of three MSCs connected in parallel increased to 3x that of a single MSC when operated at the same current density. When the three MSCs were connected in series, it exhibited a 3x higher voltage window with a similar discharge time at the same current density. An alternative way to increase the voltage output is to make the asymmetric MSCs.$^{27}$ Here, asymmetric MSCs of LIG-FeOOH//LIG-MnO$_2$ were constructed using LIG-FeOOH in the negative electrodes (Figure 1.20 and Figure 1.21) and LIG-MnO$_2$ in the positive electrodes (Figure 1.22, Figure 1.23 and Figure 1.24) while PVA/LiCl was used as the solid-state electrolyte.

**Figure 1.18. Volumetric specific capacitance of LIG-PANI.**

![Volumetric specific capacitance of LIG-PANI](image)
Figure 1.19. Assembling of multiple devices in parallel and series configurations.
(a) A digital image of three fabricated devices on a single PI sheet. (b) Three single devices in parallel and series wiring schemes, respectively. (c) Galvanostatic charge discharge curves of LIG-MnO$_2$-2.5h in single and parallel at a current density of 2.0 mA cm$^{-2}$ and comparison with a single device. (d) Galvanostatic charge discharge curves of LIG-MnO$_2$-2.5h in single and series at a current density of 2.0 mA cm$^{-2}$. (e) Galvanostatic charge discharge curves of LIG-PANI-15 in single and parallel device at a current density of 2.0 mA cm$^{-2}$. (f) Galvanostatic charge discharge curves of LIG-PANI-15 in single and series at a current density of 2.0 mA cm$^{-2}$. 
Figure 1.20. Cyclic voltammetry curves of LIG-FeOOH. (a) LIG, (b) LIG-FeOOH-1.0h, (c) LIG-FeOOH-1.5h, and (d) LIG-FeOOH-2.0h over a scan rate range of 10 and 100 mV s$^{-1}$ in the potential window from 0 to -0.8 V (vs Ag/AgCl).
Figure 1.21. Galvanostatic charge discharge curves of LIG-FeOOH. (a) LIG, (b) LIG-FeOOH-1.0h, (c) LIG-FeOOH-1.5h, and (d) LIG-FeOOH-2.0h over a current density range of 0.5 to 10 mA cm$^{-2}$ in the potential window from 0 to -0.8 V (vs Ag/AgCl). (e) Areal specific capacitance of LIG, LIG-FeOOH-1.0h, LIG-FeOOH-1.5h, and LIG-FeOOH-2.0h over a current density range of 0.5 and 10 mA cm$^{-2}$.

The loading amount of negative and positive electrodes in the asymmetric MSCs should be balanced in order to obtain the best cell performance. Therefore, the charges on the negative electrode ($Q$) should be equal to the charges on the positive electrode ($Q_r$). The charge stored at the negative electrode is determined by: $Q = C_{\text{negative}} \times A_{\text{negative}} \times V_{\text{negative}} \times H_{\text{negative}}$, where $C_{\text{negative}}$ is the specific capacitance of the negative electrode, $V_{\text{negative}}$ is the applied voltage, $A_{\text{negative}}$ is the area value of the negative electrode, and $H_{\text{negative}}$ is the height of the negative electrode. The charge stored at the positive electrode is determined by: $Q_r = C_{\text{positive}} \times A_{\text{positive}} \times V_{\text{positive}} \times H_{\text{positive}}$, where $C_{\text{positive}}$ is the specific capacitance of the positive electrode, $V_{\text{positive}}$ is the applied voltage, $A_{\text{positive}}$ is the area value of the positive electrode, and $H_{\text{positive}}$ is the height of the positive electrode. In this asymmetric MSCs, LIG-MnO$_2$-X work as positive electrodes. LIG-MnO$_2$-1.0h showed high charge amount compared to LIG-FeOOH-X. Therefore, we reduced the deposition time in order to match that of the negative electrodes.
Figure 1.22. Cyclic voltammetry curves of LIG-MnO$_2$ with short deposition time. (a) LIG, (b) LIG-MnO$_2$-0.14h, (c) LIG-MnO$_2$-0.27h, (c) LIG-MnO$_2$-0.56h, and (e) LIG-MnO$_2$-0.83h over a scan rate range of 10 and 100 mV s$^{-1}$ in the potential window from 0 to 1.0 V (vs Ag/AgCl).
Figure 1.23. Galvanostatic charge discharge curves of LIG-MnO₂ with short deposition time.
(a) LIG, (b) LIG-MnO₂-0.14h, (c) LIG-MnO₂-0.27h, (c) LIG-MnO₂-0.56h, and (e) LIG-MnO₂-0.83h over a current density range of 0.5 to 10 mA cm⁻² in the potential window 0 to 1.0 V (vs Ag/AgCl). (f) Areal specific capacitance of LIG, LIG-MnO₂-0.14h, LIG-MnO₂-0.27h, LIG-MnO₂-0.56h, and LIG-MnO₂-0.83h over a current density range of 0.5 and 10 mA cm⁻².

Figure 1.24. Cross-sectional SEM image of LIG-MnO₂-0.27h, showing the height of ~ 40 µm. The scale bar is 100 µm.

LIG-MnO₂-X work as positive electrodes in the asymmetric MSCs. The electrochemical performance of LIG-MnO₂-X are also studied in the same three-electrode system. Figure 1.22 shows the CV curves of LIG and LIG-MnO₂-X at different scan rates of 10 to 100 mV s⁻¹ in the potential window of 0 to 1.0 V (vs Ag/AgCl). The curve from LIG alone is nearly negligible, again demonstrating little
contribution in capacitance from LIG in the composite of LIG-MnO$_2$-X, which is consistent with the CV analysis in two-electrode.

**Figure 1.23** shows the galvanostatic charge-discharge curves of LIG and LIG-MnO$_2$-X at a current density of 0.5 to 10 mA cm$^{-2}$. All these samples show the almost symmetrical charging and discharging curves and small voltage drops at initial discharge states, indicating the good capacitive behavior and high conductivity. Based on these curves, the areal specific electrode capacitance of these samples are plotted as shown in **Figure 1.23**$^f$ ($C_{\text{positive}} = 4I / (A_{\text{positive}} \times (dV/dt))$, where $I$ is the current applied, $A_{\text{positive}}$ is the total area of the electrode, and $dV/dt$ is the slope of the discharge curve). The specific capacitance of LIG-MnO$_2$-X increases with the increase of the MnO$_2$ amount in the LIG-MnO$_2$-X. LIG-MnO$_2$-0.27h well-matches LIG-FeOOH-1.5h in the amount charge. Therefore, they were chosen as positive and negative electrodes assembling the asymmetric MSCs, defined as LIG-FeOOH/\LIG-MnO$_2$.

**Figure 1.25a** shows the CV curves of LIG-FeOOH/\LIG-MnO$_2$ at different scan rates in the potential window of 0 to 1.8 V. Its nearly rectangular CV shape is indicative of good capacitive behavior. This is further supported by the triangular galvanostatic charge discharge curves in the same potential window as shown in **Figure 1.25b**. The working voltage increased from 1.0 V in the case of LIG-MnO$_2$ symmetric MSCs to 1.8 V in LIG-FeOOH/\LIG-MnO$_2$ asymmetric MSCs. One of the asymmetric MSCs can power a light emitting diode (LED) (1.7 V, 30 mA) (**Figure 1.26**). Capacitance of the asymmetric MSCs is calculated based on charge discharge curves in **Figure 1.25b** and **Figure 1.27**. Areal and volumetric capacitances of LIG-
FeOOH//LIG-MnO₂ (full device capacitance) are 21.9 mF cm⁻² and 5.4 F cm⁻³, respectively, at a current density of 0.25 mA cm⁻² (Figure 1.25c). When the current density increases to 10 mA cm⁻², 64 % capacitance retention is seen. MSCs of LIG-MnO₂-2.5h, LIG-PANI-15, and LIG-FeOOH//LIG-MnO₂ also showed high galvanostatic capacitance as shown in Figure 1.28. The cycling life of LIG-FeOOH//LIG-MnO₂ is also evaluated by the extended galvanostatic charge discharge cycles. As shown in Figure 1.25d, 84% capacitance is retained after 2000 cycles, demonstrating a promising cycling stability.

Figure 1.25. Electrochemical performance of LIG-FeOOH//LIG-MnO₂ asymmetric MSCs. (a) CV curves of LIG-FeOOH//LIG-MnO₂ at a scan rate range of 10 to 100 mV s⁻¹. (b) Galvanostatic charge discharge curves of LIG-FeOOH//LIG-MnO₂ at a current density range of 0.25 to 4.0 mA cm⁻². (c) Areal and volumetric specific capacitance of LIG-FeOOH//LIG-MnO₂ over a current density range of 0.25 and
10 mA cm$^{-2}$. (d) Cycling stability of LIG-FeOOH//LIG-MnO$_2$ at the current density of 1.0 mA cm$^{-2}$.

Figure 1.26. Digital image of one LED (1.7 V, 30 mA) lit by one asymmetric MSC of LIG-FeOOH//LIG-MnO$_2$. 
Figure 1.27. Galvanostatic charge discharge curves of LIG-FeOOH//LIG-MnO\textsubscript{2}. Over a current density range of 5.0 to 10 mA cm\textsuperscript{-2} in the potential window 0 to 1.8 V.

![Galvanostatic charge discharge curves](image)

Figure 1.28. Galvanostatic capacitance calculated by mass of the MSCs. (a) LIG-MnO\textsubscript{2}-2.5h, (b) LIG-PANI-15, and (c) LIG-FeOOH//LIG-MnO\textsubscript{2}. The device capacitance was obtained based on the total mass of LIG and MnO\textsubscript{2}, PANI, and FeOOH, respectively.

The flexibility of MSCs from LIG-MnO\textsubscript{2}-2.5h, LIG-PANI-15, and LIG-FeOOH//LIG-MnO\textsubscript{2} was also studied as shown in Figure 1.29. The digital image of one MSC device that is manually bent with a bending angle ($\alpha$\textsubscript{B}) of $\sim$ 135° is show in Figure 1.29a. The CV curves at different $\alpha$\textsubscript{B} are nearly overlapping with each other, and the calculated capacitance remains almost the same, indicating the stable performance of LIG-MnO\textsubscript{2}, LIG-PANI, and LIG-FeOOH//LIG-MnO\textsubscript{2} at these states. The flexibility tests carried out by bending the device with a $\alpha$\textsubscript{B} of $\sim$ 90° (Figure 1.29e) show a good mechanical flexibility of these materials with only 10% capacitance decay after 10000 bending cycles. The good mechanical flexibility is further proved by the well-maintained morphologies of LIG-MnO\textsubscript{2}-2.5h after bending test (Figure...
compared to the original one (Figure 1.5). Some small increase in performance at early cycles can be attributed to enhanced electrolyte penetration into the LIG-PANI-15. These results demonstrate that all three of the MSCs, LIG-MnO$_2$-2.5h, LIG-PANI-15, and LIG-FeOOH//LIG-MnO$_2$, are effective flexible MSCs.
Figure 1.29. Flexibility testing of LIG-MnO$_2$-2.5h, LIG-PANI-15, and LIG-FeOOH//LIG-MnO$_2$.
(a) Digital photograph of a device under bending. The angle labeled as $\alpha_B$ in the image is defined as the bending angle. CV curves and capacitance retention of (b) LIG-MnO$_2$-2.5h, (c) LIG-PANI-15, and (d) LIG-FeOOH//LIG-MnO$_2$ under bending angles of 0°, 45°, 90°, 135°, and 180° at a scan rate of 40 mV s$^{-1}$. (e) Capacitance retention of LIG-MnO$_2$-2.5h, LIG-PANI-15, and LIG-FeOOH//LIG-MnO$_2$ at different bending cycles with a $\alpha_B$ of $\sim$90°.

Figure 1.30. Cross-sectional SEM images of MSCs of LIG-MnO$_2$-2.5h after 10000 times bending test with a $\alpha_B$ of $\sim$90°.
Figure 1.31. Ragone plots of LIG-MnO$_2$-2.5h, LIG-PANI-15, and LIG-FeOOH//LIG-MnO$_2$.

Volumetric energy and power density of LIG-MnO$_2$-2.5h, LIG-PANI-15, and LIG-FeOOH//LIG-MnO$_2$, and their comparison with commercially available energy storage devices. The data for the Li thin-film battery, Al electrolytic capacitor, commercial SC and AC-SC were reproduced from literature references.$^9,^{24,35,36}$

Unlike traditional supercapacitors where the performance is evaluated per weight of the active material, the footprint area of MSCs becomes the key consideration, making the spacial energy and power density the most important performance metrics.$^{37}$ Figure 1.31 and Figure 1.32 show the Ragone plots demonstrating the areal and volumetric energy and power density of LIG-related MSCs and their comparison with commercially available energy storage devices. Among the LIG-MnO$_2$-MSCs, the highest energy densities are 32.4 µWh cm$^{-2}$ and 3.2 mWh cm$^{-3}$, which is an increase of >1200 and >290 times, respectively, compared with LIG at a current density of 0.5 mA cm$^{-2}$ (Table 1.1). For LIG-PANI-SCs, the highest energy densities are 8.0 µWh cm$^{-2}$ and 1.1 mWh cm$^{-3}$, which are 41 and 15 times higher, respectively, than that of LIG at a current density of 0.5 mA cm$^{-2}$ (Table 1.1). For LIG-FeOOH//LIG-MnO$_2$, they are 9.6 µWh cm$^{-2}$ and 2.4 mWh cm$^{-3}$, respectively. Such energy densities from LIG-MnO$_2$, LIG-PANI, and LIG-FeOOH//LIG-MnO$_2$ are much higher than some typical commercial supercapacitors (SCs) (2.75 V/44 mF and 5.5 V/100 mF), and even comparable to Li thin-film batteries (4 V/500 µAh).$^{38}$ The maximum areal and volumetric power densities are 2334 µW cm$^{-2}$ and 298 mW cm$^{-3}$ for LIG-MnO$_2$, 649 µW cm$^{-2}$ and 1511 mW cm$^{-3}$ for LIG-PANI, and 11853 µW cm$^{-2}$ and 2891 mW cm$^{-3}$ for FeOOH//LIG-MnO$_2$, are comparable to commercial...
SCs, and > 100 times higher than in Li thin-film batteries. The performance of these MSCs show much better performance than our previously studied LIG-MSCs and boron doped LIG-MSCs in aqueous or polymeric acidic electrolyte (Figure 1.33),\textsuperscript{28-30} and also better performance than most other reported carbon and pseudocapacitive materials.\textsuperscript{1} Among most of the recent reported results, high-cost lithography for electrode patterning and high temperature and multi-step synthetic processes are often required. In this work, the synthesis and patterning of LIG are simultaneously achieved in the first step, and both the laser induction step and subsequent electrodepositions are done under mild temperature and ambient atmosphere.
Figure 1.32. Ragone plots of LIG-MnO$_2$, LIG-PANI, and LIG-FeOOH//LIG-MnO$_2$. 
Figure 1.33. Comparison of the volumetric energy density of LIG-derived MSCs.

Table 1.1. Electrochemical performances of MSCs of LIG-MnO$_2$ and LIG-PANI devices.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Electrolyte</th>
<th>Specific capacitance*</th>
<th>Energy density*</th>
<th>Power density*</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIG-PANI-1.5</td>
<td>PVA/H$_2$SO$_4$</td>
<td>960.8</td>
<td>47.5</td>
<td>8.0</td>
</tr>
<tr>
<td>LIG-PANI-1.0</td>
<td>PVA/H$_2$SO$_4$</td>
<td>250.1</td>
<td>45.0</td>
<td>5.6</td>
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<tr>
<td>LIG-PANI-5</td>
<td>PVA/H$_2$SO$_4$</td>
<td>153.3</td>
<td>41.0</td>
<td>1.0</td>
</tr>
<tr>
<td>LIG</td>
<td>PVA/H$_2$SO$_4$</td>
<td>8.4</td>
<td>1.8</td>
<td>1.9×10$^{-1}$</td>
</tr>
<tr>
<td>LIG-MnO$_2$-4.0h</td>
<td>PVA//UCI</td>
<td>933.6</td>
<td>92.4</td>
<td>32.4</td>
</tr>
<tr>
<td>LIG-MnO$_2$-3.0h</td>
<td>PVA//UCI</td>
<td>799.6</td>
<td>83.3</td>
<td>27.8</td>
</tr>
<tr>
<td>LIG-MnO$_2$-2.5h</td>
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<td>623.8</td>
<td>70.1</td>
<td>21.7</td>
</tr>
<tr>
<td>LIG-MnO$_2$-2.0h</td>
<td>PVA//UCI</td>
<td>524.2</td>
<td>63.2</td>
<td>18.2</td>
</tr>
<tr>
<td>LIG-MnO$_2$-1.5h</td>
<td>PVA//UCI</td>
<td>339.4</td>
<td>44.7</td>
<td>11.8</td>
</tr>
<tr>
<td>LIG-MnO$_2$-1.0h</td>
<td>PVA//UCI</td>
<td>229.0</td>
<td>30.2</td>
<td>8.0</td>
</tr>
<tr>
<td>LIG</td>
<td>PVA//UCI</td>
<td>0.8</td>
<td>1.7×10$^{-1}$</td>
<td>2.7×10$^{-1}$</td>
</tr>
<tr>
<td>LIG-FeOOH//LIG-MnO$_2$</td>
<td>PVA//UCI</td>
<td>21.9</td>
<td>5.4</td>
<td>9.9</td>
</tr>
</tbody>
</table>

Notes: * The specific capacitance and the energy density was calculated at the current density of 0.5 mA cm$^{-2}$. b The power density of these samples was obtained at 20.0 mA cm$^{-2}$ for LIG-PANI, and 8.0 mA cm$^{-2}$ for LIG-MnO$_2$, and 10.0 mA cm$^{-2}$ for LIG-FeOOH//LIG-MnO$_2$. c The capacitance of LIG-FeOOH//LIG-MnO$_2$ is the device capacitance, not the specific capacitance of the electrodes.
1.2.3. **Conclusion**

We have demonstrated a simple route to make an all-solid-state flexible MSCs with interdigitated electrodes using a hybrid composite of LIG. The room temperature and ambient air-based laser induction is followed by MnO$_2$, FeOOH, or PANI electrodeposition. The solid-state flexible symmetric MSCs of LIG-MnO$_2$ and LIG-PANI, and asymmetric MSCs of LIG-FeOOH//LIG-MnO$_2$, demonstrate high specific capacitances, promising energy and power densities, and excellent cycling stabilities and mechanical flexibilities. These findings not only simplify device fabrication processes with easy control of the size of devices and scalability, but also demonstrate the applicability of the LIG technique to a wide range of other pseudocapacitive materials, beyond that of MnO$_2$, FeOOH, and PANI. Therefore, the design strategy developed here opens a new avenue for very simply constructing high performance, all-solid-state flexible MSCs.

1.3. **Experimental Contributions**

**Jibo Zhang** designed part of the experiments, fabricated the MSCs, carried out the electrochemical characterization and data analysis of the MSCs. **Lei Li** designed part of the experiments, performed the Raman, XRD, XPS, and data analysis of the MSCs, and prepared the manuscript. **Zhiwei Peng** designed part of the experiments, performed the TEM, SEM images and data analysis.
2.1. Introduction

The use of renewable energy sources, including wind and solar energies for the generation of electricity, is a topic of much research.\textsuperscript{40-43} This electricity can be supplied to users through power lines, if they exist. Oftentimes, the wind or solar-generated power is distant from users and building power lines is expensive; if the power lines exist, losses occur in transmission. The electricity is also irregular in its supply depending on the weather and the time of day. Storage of the electricity at the point of generation would have many benefits. However, the electricity generated is not easily stored in the large quantities needed to supply grid-level energy needs because of the limitations of present-day batteries. Hence, conversion of the electricity supply into a chemical fuel source is beneficial so that the energy can be stored in chemical bonds, and shipped as required.\textsuperscript{44-46} Among the clean-energy
methods to accomplish that task is the splitting of water to H\(_2\) and O\(_2\).\(^{47, 48}\) Not only can these products be combusted back into water, thereby affording energy with no subsequent CO\(_2\) emissions, but they can be used in fuel cells that are significantly more efficient than combustion engines. However, the sluggish kinetics of hydrogen and oxygen evolution reactions (HER and OER, respectively) in water splitting requires catalysts to increase the efficiencies.\(^{49-51}\) Apart from the noble metal materials such as Pt, RuO\(_2\) and IrO\(_2\), numerous noble-metal-free catalysts have been developed.\(^{52, 53}\) For example, transition-metal carbides,\(^{54-56}\) phosphides\(^{57, 58}\) and sulfides\(^{59, 60}\) have shown favorable performance in HER. The oxides/hydroxides of cobalt,\(^{61}\) nickel,\(^{62}\) manganese\(^{63}\) and iron\(^{64}\) also have proven to be efficient catalysts for OER. However, for the scalable production of H\(_2\) and O\(_2\), the catalytic electrodes should be easily fabricated to minimize their overall cost. It is therefore desirable to couple the HER and OER processes into a single simple package.

Laser-induced graphene (LIG) is a 3D porous graphene material fused to a flexible substrate that is prepared by a one-step laser scribing process on commercial polyimide (PI, with a trade name Kapton) film.\(^{28}\) The LIG on PI has high porosity and is easily formed in the air at room temperature in a scalable production route. It is low cost, has high electrical conductivity and good chemical stability. While LIG has been used for direct patterning applications in microsupercapacitors and related devices,\(^{1, 29, 30, 65}\) in this study we exploit the LIG process to fabricate efficient catalytic electrodes for splitting water to H\(_2\) and O\(_2\) starting from a single sheet of plastic. A CO\(_2\) laser is used to convert PI into LIG with a predetermined pattern. The active
species are either formed \textit{in situ} in the LIG-forming process by having Pt nanoparticles impregnated in the starting PI film, or by subsequent electodeposition of Ni$_{x}$Fe$_{y}$(OH)$_{2x+3y}$ or CoP/Co$_3$(PO$_4$)$_2$ onto the LIG.\textsuperscript{66,67} The high porosity and electrical conductivity of LIG facilitates efficient contact and charge transfer with the requisite electrolyte. The LIG-based electrodes exhibit high HER and OER performance with excellent long-term stability. The overpotential to reach 100 mA cm$^{-2}$ for HER and OER is as low as 214 and 380 mV with relatively low Tafel slopes of 54 and 49 mV dec$^{-1}$, respectively. Additionally, the catalytic electrodes are prepared on either side of the PI sheet, then the device is assembled with an O-ring setup. By serial connection of the electrodes with a power source, H$_2$ and O$_2$ are simultaneously generated on either side of the plastic sheet at a current density of 10 mA cm$^{-2}$ upon 1.66 V, and thereby selectively captured, providing a promising route to efficient and complete water splitting.

\textbf{2.2. Efficient Water-Splitting Electrodes Based on Laser-Induced Graphene}

\textbf{2.2.1. Experimental Section}

\textbf{2.2.1.1. Device Fabrication}

\textbf{Preparation of LIG-Pt.} Poly(pyromellitic dianhydride-co-4,4’-oxidianiline amic acid) (7.8 g) solution (12.8 wt % in N-methyl-2-pyrrolidone (NMP)/aromatic solvent, 80:20, 25038-81-7, Sigma-Aldrich) was used as a precursor solution for
formation of a PI sheet. Pt(II) acetylacetonate (15170-57-7, Sigma-Aldrich) (50 mg, 0.13 mmol) was dissolved in 1 mL of NMP and then added to the PAA solution with bath sonication (Cole Parmer, model 08849-00) for 2 h to form a homogeneous mixture. The solution was poured into an aluminum dish (~5 cm in diameter) and then placed in a vacuum oven (~120 mm Hg) at 60 °C 3 d to remove the solvent. The film-imidization process was completed in an oven at 240 °C for 30 min and then 300 °C for another 30 min. LIG was generated by a CO₂ laser cutter system (Universal XLS10MWH laser cutter platform) on the Pt doped PI film using 3% of the full power (75 W) and 5% of the full speed. The gas flow of H₂ (3%)/Ar was maintained during the laser scribing process. LIG was patterned into a rectangle of 5 × 6 mm². After that, Pelco colloidal Ag paint (No. 16034, Ted Pella) was applied on one side of the LIG pattern (5 × 1 mm²) to improve the conductivity. The electrodes were then connected with conductive Cu tape. A Kapton PI tape was employed followed by an epoxy (Machineable-fast set, Reorder # 04002, Hardman) sealing to protect the common areas of the electrodes. The geometrical area of the LIG electrode is 5 × 5 mm². The fabricated LIG-Pt device was stored in a vacuum desiccator (~120 mm Hg) at room temperature for future test. An electrochemical workstation was employed for further deposition or testing.

**Preparation of LIG-NiFe.** All samples were prepared under room temperature and ambient air. Kapton® PI films (McMaster-Carr, Cat. No. 2271K3, thickness: 0.005”) were used as received. LIG was generated by a CO₂ laser cutter system (Universal XLS10MWH laser cutter platform) on the Kapton® polyimide film.
using 3% of full power (75 W) and 5% of full speed in air. The fabrication of LIG electrode was prepared as described above. Then the deposition of the active material on the LIG was carried out in a 3-three electrode configuration, with Ag/AgCl as the reference electrode and a Pt plate as the counter electrode. The electrolyte bath contained 3 mM Ni(NO$_3$)$_2$·6H$_2$O and 3 mM Fe(NO$_3$)$_3$·9H$_2$O. The deposition was done at a constant potential of -1.0 V (vs Ag/AgCl) at room temperature. The optimized deposition time was 150 s. The LIG-NiFe device was stored in a vacuum desiccator (~120 mm Hg) at room temperature for future test.

**Preparation of LIG-Co-P.** The LIG electrodes were prepared in the same way as the LIG-NiFe electrodes. The deposition of active material on LIG was carried out in a 3-three electrode configuration, with Ag/AgCl as the reference electrode and a Pt plate as the counter electrode. The electrolyte bath contained 50 mM CoCl$_2$, 0.5 M NaH$_2$PO$_2$, and 0.1 M NaOAc. The deposition was done by consecutive linear scans between -0.3 and -1.0 V (vs Ag/AgCl) at a scan rate of 5 mV s$^{-1}$ for 10 cycles. The LIG-Co-P device was stored in a vacuum desiccator (~120 mm Hg) at room temperature for future testing.

**2.2.1.2. Device Characterization**

**General characterization.** SEM images were obtained on a FEI Quanta 400 high-resolution field emission SEM. TEM images were obtained by a JEOL 2100F field emission gun transmission electron microscope. The electrochemical measurements were carried out in a three-electrode configuration using a CHI 608D workstation. Pt
plate and Hg/HgO (in 1M KOH) were used as the counter and reference electrode, respectively. All tests were done in 1M KOH with 95% iR compensation. For the Hg/HgO electrode, $E_{\text{vs RHE}} = E_{\text{vs Hg/HgO}} + 0.930 \text{ V in 1M KOH}$.

### 2.2.2. Result and Discussion

Catalytic LIG electrodes are fabricated as illustrated in Figure 2.1 using a commercial laser system as found in most machine shops for cutting metal or wood patterns. The CO$_2$ laser patterns the PI film to form LIG which is further assembled to devices with an active area of $5 \times 5 \text{ mm}^2$. The catalysts are either loaded by \textit{in situ} doping such as LIG-Pt, or electrochemical deposition such as LIG-NiFe and LIG-Co-P.$^{66,67}$ The procedures are summarized in the experimental section.
Figure 2.1. The fabrication process of catalytic LIG electrodes. (a) Fabrication process of the LIG-Pt. Pt(II) acetylacetone was mixed with polyamic acid at 5 wt%. The solution was vacuum dried and cast into film, then cured in an oven. Laser scribing was done in H$_2$/Ar atmosphere to form Pt-doped LIG, followed by the device fabrication. (b) Fabrication process of the LIG-NiFe and the LIG-Co-P. LIG was directly patterned on a commercially available Kapton film with subsequent device fabrication. Then the catalysts were electrochemically deposited on the LIG to give LIG-NiFe and LIG-Co-P.

The LIG-Pt is prepared by direct laser writing on the Pt(II) acetylacetone doped PI film in a H$_2$/Ar atmosphere. The LIG-Pt possesses a 3D porous structure as illustrated in Figure 2.2 and Figure 2.3. The LIG structure is maintained through the laser process as demonstrated by the characteristic Raman peaks shown in Figure
2.4 The laser spot induces very high local temperature to carbonize the PI and simultaneously thermally reduce Pt(II) to Pt(0) under the protection of a H\textsubscript{2}/Ar atmosphere. The Pt nanoparticles are formed in situ and evenly distributed within the LIG domains with uniform size (Figure 2.2b). Figure 2.5 shows the XPS survey spectra of LIG-Pt and Figure 2.2c shows the X-ray photoelectron spectroscopy (XPS) spectrum of the LIG-Pt in Pt 4f region. The well separated spin-orbit components (Δ = 3.35 eV) at 71.13 and 74.48 eV from Pt(0) indicates the Pt(II) has been mostly reduced to Pt(0) that forms the nanoparticles and contributes to the HER (see below).
Figure 2.2. Characterizations of LIG-Pt.
(a) SEM and (b) TEM images of LIG-Pt. (c) XPS spectrum of Pt 4f region of LIG-Pt. (d) LSV of LIG-Pt for HER at a scan rate of 5 mV s\(^{-1}\). Inset: corresponding Tafel plots of LIG-Pt. All tests are done in 1 M KOH with 95% iR compensation.
Figure 2.3. TEM and SEM images of LIG-Pt. (a, b) TEM and (c, d) top view SEM images of LIG-Pt at different magnifications.
Figure 2.4. Raman spectrum of LIG-Pt.

Figure 2.5. XPS survey spectrum of LIG-Pt.
Figure 2.6. SEM images of LIG-NiFe.

The LIG-NiFe and LIG-Co-P are fabricated by laser writing on commercial Kapton film followed by the electrodeposition of catalysts (Figure 2.1). The potentiostat deposition of LIG-NiFe is done in a bath solution containing Ni$^{2+}$, Fe$^{3+}$ and NO$_3^-$ ions are reduced at the negative potential (-1.0 V vs Ag/AgCl) to form NH$_4^+$ and OH$^-$. The bimetallic hydroxide of Ni and Fe (Ni$_x$Fe$_y$(OH)$_{2x+3y}$) forms on the LIG surface. Due to the high catalytic activity of Ni$_x$Fe$_y$(OH)$_{2x+3y}$ an optimized deposition time of 150 s is preferred. Since the loading
of the catalyst is quite low, the morphology of LIG-NiFe resembles that of the pristine LIG as demonstrated by the porous surface with lined structure induced by laser writing (Figure 2.6). The thickness of the active layer is 60 μm. The XPS spectra of LIG-NiFe are shown in Figure 2.7. The Ni 2p peak at 855.9 eV and Fe 2p peak at 710.9 eV suggests the formation of hydroxide (Ni_{x}Fe_{y}(OH)_{2x+3y}) by electrodeposition, and the atomic ratio of Ni^{2+} to Fe^{3+} is 3:4.

Figure 2.7. XPS spectra of LIG-NiFe.
The Co-P-derived electrode LIG-Co-P is prepared by potentiodynamic electrodeposition. The transmission electron microscopy (TEM) images (Figure 2.8) of LIG-Co-P shows the \( \text{Co}_3(\text{PO}_4)_2 \) and CoP nanoparticles are well-embedded in the LIG domains. The scanning electron microscopy (SEM) images in Figure 2.9 demonstrate the rough surface of the LIG-Co-P with a thickness of 55 µm fused to the underlying PI film. The LIG-Co-P retains the striped pattern induced by the laser raster scanning, with a large number of clusters on the surface as seen at higher magnification (Figure 2.9). The elemental mapping of the as prepared electrode reveals the elemental composition of the clusters to be C, Co, O and P (Figure 2.10). The Co 2p and P 2p XPS spectra (Figure 2.11) show the details of the anticipated components. The Co 2p\(_{3/2}\) core level region has two main peaks at 778.4 and 781.9 eV with two satellites at 785.2 and 786.6 eV, respectively. The 778.4 eV peak is very close to that of metallic Co. The high P 2p spectrum shows three main peaks at 129.7 and 133.3 eV. The 129.7 eV peak of P and 778.4 eV peak of Co 2p\(_{3/2}\) are associated with the typical binding energies of Co 2p and P 2p in CoP. The P 2p peak at 133.3 eV originates from the \( \text{PO}_4^{3-} \) species, indicating the existence of \( \text{Co}_3(\text{PO}_4)_2 \) in consideration of the Co 2p peak at 781.9 eV. The performance of the catalytic LIG electrodes should benefit from the well distributed catalysts on the porous conductive material.
Figure 2.8. TEM images of LIG-Co-P and pristine LIG.
Figure 2.9. SEM images of images of LIG-Co-P.

Figure 2.10. Elemental mapping of as prepared LIG-Co-P.
The as-prepared LIG electrodes can be directly used for HER or OER in accordance with the activity of the catalysts using a standard three-electrode electrochemical cell. The HER catalytic activity of the LIG-Pt is evaluated as shown in Figure 2.2d by the linear-sweep voltammograms at a scan rate of 5 mV s\(^{-1}\) in 1 M KOH with 95% iR compensation. The Pt nanoparticles in LIG-Pt contribute to efficient activity as demonstrated by the nearly zero onset potential (\(\eta\)) vs RHE, after which the current density increases rapidly. The overpotentials needed to reach 10 and 100 mA cm\(^{-2}\) are 107 and 256 mV, respectively. These values are comparable to the recent published catalysts (Table 2.1). Conversely, the pristine LIG shows very poor activity for HER with \(\eta\) higher than 500 mV. It should be noted that the Tafel analysis of LIG-Pt reveals a slope of 83 mV dec\(^{-1}\), which is slightly higher than conventional Pt-based electrodes such as Pt/C and Pt wires. The reason may be that the Pt nanoparticles formed \textit{in situ} are partially covered by the LIG as indicated in Figure 2.3, and

\textbf{Figure 2.11.} XPS spectra of as-prepared LIG-Co-P in Co 2p region and P 2p region.
consequently the active sites are not fully exposed to the solution during the catalytic reaction.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Tafel Slope (mV dec(^{-1}))</th>
<th>Electrolyte</th>
<th>Current Density (mA cm(^{-2}))</th>
<th>Overpotential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIG-Pt</td>
<td>83</td>
<td>1 M KOH</td>
<td>10</td>
<td>109</td>
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<tr>
<td>LIG-Co-P</td>
<td>54</td>
<td>1 M KOH</td>
<td>10</td>
<td>141</td>
</tr>
<tr>
<td>Co-P/Cu(^{67})</td>
<td>42</td>
<td>1 M KOH</td>
<td>10</td>
<td>94</td>
</tr>
<tr>
<td>NiO/Ni-CNT(^{62})</td>
<td>51</td>
<td>1 M KOH</td>
<td>100</td>
<td>&lt;100</td>
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<tr>
<td>CoP/CC(^{72})</td>
<td>129</td>
<td>1 M KOH</td>
<td>10</td>
<td>209</td>
</tr>
<tr>
<td>Ni(_2)P(^{73})</td>
<td>205</td>
<td>1 M KOH</td>
<td>20</td>
<td>205</td>
</tr>
<tr>
<td>Co-S/FTO(^{74})</td>
<td>N/A</td>
<td>1 M KOH</td>
<td>1</td>
<td>480</td>
</tr>
<tr>
<td>MoS(_{2+x})/FTO(^{75})</td>
<td>N/A</td>
<td>1 M KOH</td>
<td>10</td>
<td>310</td>
</tr>
<tr>
<td>MoB(^{55})</td>
<td>59</td>
<td>0.1 M KOH</td>
<td>10</td>
<td>225</td>
</tr>
<tr>
<td>Ni/Ni(OH)(_2)(^{76})</td>
<td>128</td>
<td>0.1 M KOH</td>
<td>10</td>
<td>&gt;300</td>
</tr>
</tbody>
</table>

Table 2.1. Comparison of the HER electrocatalysts in alkaline media.
The LIG-NiFe exhibits significant OER activity as illustrated in Figure 2.12. Cyclic voltammetry (CV) in Figure 2.12a demonstrates the catalytic behavior of the LIG-NiFe. A pair of redox peaks are observed at ~1.35 to 1.5 V (vs RHE), corresponding to the formation of Ni with higher oxidation states such as Ni(III) and Ni(IV) species that catalyze OER.\(^77\) It can be observed from the LSV curve shown in Figure 2.12b that the anodic current of the LIG-NiFe increases sharply at ~220 mV whereas there is an overlap from the redox of Ni. A more detailed LSV of the LIG-NiFe is shown in Figure 2.13, where the scan is done in reverse to minimize the disturbance from the redox peaks. The \(\eta_{\text{OER}}\) is determined to be 230 mV and the LIG-NiFe reaches 10 and 100 mA cm\(^{-2}\) at low overpotentials of 292 and 380 mV, respectively. The pristine LIG, by contrast, does not show significant current until very high \(\eta\) (more than 400 mV) is applied.

The OER process is generally initiated by OH\(^-\) electrosorption on the electrode surface. Therefore, a high electrochemical active surface area (EASA) and a high affinity for adsorbed OH\(^-\) intermediates are the basis for an efficient OER catalyst.\(^78\) We estimate the EASA of LIG-NiFe using the CV curves measured in a non-Faradaic region at scan rates ranging from 10 to 100 mV s\(^{-1}\) as summarized in Figure 2.14.\(^79\) By plotting the current density at 0 V (vs Hg/HgO) as a function of scan rate with subsequent fitting, we calculate the double layer capacitance \((C_{\text{dl}})\) to be 1.76 mF cm\(^{-2}\) (an average of 1.79 and 1.73 mF cm\(^{-2}\) from charge and discharge currents, respectively). Remarkably, the \(C_{\text{dl}}\) value suggests that the LIG-NiFe possesses a high EASA of 11 cm\(^2\), which is 44 times higher than its geometric area of 0.25 cm\(^2\). The
affinity for OH⁻ intermediates also needs to be considered. Since the equilibrium coverage of OH⁻ intermediates on the catalytic surface is achieved quickly, the subsequent O₂ generation is the rate determining process and results in a lower Tafel slope. As calculated from Figure 2.12c, the Tafel slope of LIG-NiFe is as low as 49 mV dec⁻¹, indicating the rapid reaction kinetics on the LIG-NiFe. This value is superior to the noble metal based OER catalyst RuO₂, and is also competitive to the state-of-the-art catalysts, which is particularly noteworthy in consideration of the facile preparation process (Table 2.2). Additionally, LIG-NiFe shows good durability as shown in Figure 2.12d. After 1000 cycles of water oxidation, the overpotential to deliver a current density of 10 mA cm⁻² slightly increases from 292 to 302 mV.
Figure 2.12. Electrocatalytic performance of LIG-NiFe for OER. (a) CV curve of the LIG-NiFe at a scan rate of 10 mV s$^{-1}$. (b) LSV at a scan rate of 5 mV s$^{-1}$ and (c) corresponding Tafel plots of the LIG-NiFe. Inset: enlarged region from 1.3 to 1.5 V (vs RHE). The dashed circle shows the overlap between OER onset and the oxidation of Ni(II). (d) Stability test: LSV of the LIG-NiFe after 1000 OER cycles compared to the initial curve.

Figure 2.13. LSV of LIG-NiFe scanned from 1.65 to 1.2 V at a speed of 5 mV s$^{-1}$. The interference from the redox of Ni(II) has been eliminated and the onset potential is 230 mV.
Figure 2.14. Determination of the $C_{dl}$ of LIG-NiFe. (a) CV curves recorded at 10, 20, 40, 60, 80 and 100 mV s$^{-1}$. (b) Current density at 0 V (vs Hg/HgO) as a function of scan rate. The linear fitting reveals the $C_{dl}$ of LIG-NiFe to be 1.76 mF cm$^{-2}$ on average.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Tafel Slope (mV dec$^{-1}$)</th>
<th>Electrolyte</th>
<th>Current Density (mA cm$^{-2}$)</th>
<th>Overpotential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIG-NiFe</td>
<td>49</td>
<td>1 M KOH</td>
<td>10</td>
<td>292</td>
</tr>
<tr>
<td>LIG-Co-P</td>
<td>84</td>
<td>1 M KOH</td>
<td>10</td>
<td>364</td>
</tr>
<tr>
<td>NiCo-LDH$^{80}$</td>
<td>40</td>
<td>1 M KOH</td>
<td>10</td>
<td>367</td>
</tr>
<tr>
<td>CoCo LDH$^{81}$</td>
<td>59</td>
<td>1 M KOH</td>
<td>10</td>
<td>393</td>
</tr>
<tr>
<td>CoMn LDH$^{82}$</td>
<td>43</td>
<td>1 M KOH</td>
<td>10</td>
<td>324</td>
</tr>
<tr>
<td>NiFe-LDH/CNT$^{83}$</td>
<td>35</td>
<td>1 M KOH</td>
<td>10</td>
<td>247</td>
</tr>
<tr>
<td>Ni$<em>x$Co$</em>{3-x}$O$_4$</td>
<td>59-64</td>
<td>1 M KOH</td>
<td>10</td>
<td>370</td>
</tr>
<tr>
<td>CoO$_x$ Film$^{85}$</td>
<td>42</td>
<td>1 M KOH</td>
<td>10</td>
<td>403</td>
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<td>71</td>
<td>1 M KOH</td>
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<td>1 M NaOH</td>
<td>10</td>
<td>&gt;350</td>
</tr>
</tbody>
</table>

Table 2.2. Comparison of the OER electrocatalysts in alkaline media.
Figure 2.15. Electrocatalytic performance of the bifunctional LIG-Co-P. (a) Water electrolysis of the LIG-Co-P illustrated by the CV curves. The LSV of the LIG-Co-P for (b) HER and (c) OER. Inset: corresponding Tafel plots. (d) Stability test; LSV of the LIG-Co-P after 1000 cycles of HER and OER comparing with the initial curves, respectively.

The electrochemically deposited LIG-Co-P works as a bifunctional catalytic electrode for either HER or OER in accordance with the applied potential as shown in Figure 2.15a. We first evaluated the HER activity of the LIG-Co-P in 1 M KOH by the LSV (Figure 2.15b). The data shows that pristine LIG is relatively inert so that the catalytic activity is almost completely from the Co-P composites. The $\eta_{HER}$ of HER is
determined to be 75 mV from Figure 2.16a, and the current density reaches 10 and 100 mA cm$^{-2}$ at 141 and 214 mV, respectively. The corresponding Tafel slope for HER calculated from the LSV (Figure 2.15b) is 54 mV dec$^{-1}$. The HER process in alkaline solution is expressed by either the Volmer-Heyrovsky process or the Volmer-Tafel pathway.$^{87}$ $^{88}$ Both pathways involve the adsorption of a H$_2$O molecule and subsequent reduction of H$_2$O into adsorbed OH$^-$ and H atom.$^{78}$ The detachment of OH$^-$ to refresh the catalyst surface and the formation of adsorbed H intermediates to generate H$_2$ are essential for efficient HER. CoP is considered to facilitate such processes because of the charge imbalance between Co and P through the transfer of electron density from Co to P.$^{89}$ The locally positively charged Co centers have strong affinity to adsorb the OH$^-$ from H$_2$O decomposition whereas the P sites favor H adsorption. Therefore, the possible occupation of OH$^-$ on H sites that blocks the active sites is eliminated and H$_2$ is efficiently generated.$^{62}$ Indeed, the high $C_{dl}$ of LIG-Co-P calculated in Figure 2.17 may be caused by the high adsorption affinity to OH$^-$. The OER activity of LIG-Co-P is evaluated in the same solution as HER (1 M KOH, Figure 2.15c). The anodic current increases rapidly after approximately 1.50 V (vs RHE). The $\eta_{OER}$ is 270 mV from Figure 2.15c, and the corresponding Tafel slope is 84 mV dec$^{-1}$. The overpotential to deliver 10 and 100 mA cm$^{-2}$ are 364 and 530 mV, which are slightly higher than the LIG-NiFe. It is worth noting that the OER activity is likely from the higher oxidation states of the CoP under anodic conditions, where the Co-oxo/hydroxo site and PO$_4^{3-}$ are formed.$^{70}$ As shown in Figure 2.11 and Figure 2.18, the XPS spectra of a post-OER LIG-Co-P is significantly different from an as-
prepared electrode. The Co 2p peak at ~778 eV lessens compared to the ~781 eV peak, suggesting a transition of the original Co valence to higher oxidation states.\textsuperscript{90} Meanwhile, the P 2p peak at ~133.2 eV arising from PO\textsubscript{4}\textsuperscript{3-} becomes dominant in the post-OER LIG-Co-P with the significant decreased intensity of P species that have a binding energy of ~130 eV.\textsuperscript{91} The PO\textsubscript{4}\textsuperscript{3-} might be responsible for the effective OER kinetics, since the surface PO\textsubscript{4}\textsuperscript{3-} group has been known to assist the proton-coupled electron transfer during OER catalysis.\textsuperscript{92, 93} The synergetic effect between CoO\textsubscript{x} and Co\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} was also suggested to improve the OER performance.\textsuperscript{90, 94} The LIG-Co-P shows excellent long-term stability for both HER and OER as illustrated in Figure 2.15d. The performance was nearly unchanged after 1000 cycles of HER or OER, respectively.

![Figure 2.16. Expanded LSV of LIG-Co-P for HER and OER.](image-url)
Figure 2.17. Determination of the $C_{dl}$ of LIG-Co-P. (a) CV curves recorded at 10, 20, 40, 60, 80 and 100 mV s$^{-1}$. (b) Current density at 0 V (vs Hg/HgO) as a function of scan rate. The linear fitting reveals the $C_{dl}$ of LIG-Co-P to be 32.50 mF cm$^{-2}$ on average.

Figure 2.18. XPS spectra of LIG-Co-P after OER test.
Figure 2.19. Illustration of the integration of catalytic LIG electrodes as a water electrolyzer. 
(a) Schematic drawing of an integrated LIG device. (b) LSV curve of the electrolyzer in 1 M KOH with 95% IR compensation. (c) A photograph of the electrolyzer working at 50 mA cm$^{-2}$. Bubbles are the generated H$_2$ (left side) and O$_2$ (right side) as depicted.

The accessibility of catalytic LIG electrodes enables full water splitting from one piece of PI film with HER and OER catalysts formed on either side as shown in Figure 2.19a. In the prototype electrolyzer, LIG is patterned on both sides of a PI film and then fabricated into LIG-Co-P and LIG-NiFe on respective sides. The migration of
OH\textsuperscript{-} is enabled by a small pinhole located at the end of the film, which might later be coated by an ion exchange membrane for large scale applications.

A preliminary investigation on the LIG electrolyzer for full water splitting was carried out in 1 M KOH. As expected, the LIG electrolyzer exhibits both efficient HER and OER activity. The LIG-Co-P works for HER and LIG-NiFe for OER, simultaneously, to deliver a current density of 10 mA cm\textsuperscript{-2} at 1.66 V as illustrated in Figure 2.19b. The current density can be further increased to 400 mA cm\textsuperscript{-2} at 1.9 V without degradation of the electrolyzer. The full water splitting performance is comparable and even better than many recently reported systems.\textsuperscript{95-97} More importantly, the PI film serves as an inherent separator for water splitting, wherein the H\textsubscript{2} comes out of one side at the same time as O\textsubscript{2} from the other side of the same device. The device is rigged in a simple O-ring system as shown in Figure 2.19c, such that the gasses that evolve are separated: H\textsubscript{2} into one tube and O\textsubscript{2} into the other, and can therefore can be stored separately. Figure 2.20 and Figure 2.21 illustrate the long-term stability of the LIG electrolyzer. Supplementary videos (Video 2.1, Video 2.2 and Video 2.3) show the real-time water splitting by the LIG electrolyzer working at 50 mA cm\textsuperscript{-2}. Large amount of H\textsubscript{2} and O\textsubscript{2} bubbles form immediately when a potential is applied, demonstrating the high catalytic activity of LIG electrolyzer. The facile fabrication and easy tunability of LIG electrolyzer also favors other catalysts that can be simply loaded onto LIG.
Figure 2.20. Additional test for the single-sheet with pinhole and O-ring setup electrolyzer in 1 M KOH with 95% iR compensation. LSV of the electrolyzer compared with that of the device tested in a beaker. The LSV are nearly the same indicating that any mass transport restriction did not significantly affect the HER and OER on either side.

Figure 2.21. Stability test of the electrolyzer at 10 mA cm$^{-2}$. 
The sudden spikes in the potential were caused by the accumulation and release of bubbles that adsorbed on the electrode, which caused a decrease or increase in the effective surface area.

https://www.youtube.com/watch?v=UeJIrfAWIgw

Video 2.1. The LIG water splitting device working at 50 mA cm$^{-2}$ in a prototype O-ring setup.

https://www.youtube.com/watch?v=7tfGfVTe6QI

Video 2.2. HER electrode working at 50 mA cm$^{-2}$ in the O-ring setup.

https://www.youtube.com/watch?v=riVesb3QLec

Video 2.3. OER electrode working at 50 mA cm$^{-2}$ in the O-ring setup.

2.2.3. Conclusion

In summary, catalytic LIG electrodes are fabricated on inexpensive plastic films with catalysts loaded by either in situ doping or electrochemical deposition. The LIG electrodes, LIG-Pt, LIG-NiFe and LIG-Co-P, show superior activity to state-of-the-art catalysts for HER and OER in alkaline medium. The integration of LIG electrodes further permits full splitting of water into H$_2$ and O$_2$ using just one piece of plastic film. The straightforward and convenient fabrication of catalytic LIG electrodes demonstrated here not only provide a practical solution for H$_2$ and O$_2$ production that
can drive a fuel cell. But it might also serve as a harbinger for constructing efficient
devices for other electrocatalytic processes such as CO₂ reduction and O₂ reduction.

2.3. Experimental Contributions

**Jibo Zhang** designed the experiments, fabricated the devices, carried out the
Raman, XPS, electrochemical characterization and data analysis. **Yilun Li** and **Junwei
Sha** helped in the TEM and SEM images. **Chenhao Zhang** and **Huilong Fei** helped in
the data analysis.
Chapter 3

Oxidized Laser-Induced Graphene for Efficient Oxygen Electrocatalysis

This chapter was entirely copied from reference.98

3.1. Introduction

The ever-increasing demand for clean energy has led to extensive research on the development of renewable energy technologies,99-101 such as fuel cells,46, 102 hydrogen and oxygen production from water splitting,95, 103, 104 and rechargeable metal-air batteries.105, 106 The underlying chemical processes, including the oxygen evolution reaction (OER), hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR), generally suffer from slow kinetics.107 Effective catalysts are necessary to accelerate the reactions. Noble metals and metal oxides, such as Pt, RuO$_2$ and IrO$_2$ are known to be very efficient.108-110 However, the high cost and scarcity of the raw materials for these catalysts have slowed their mass production and commercialization. The design and synthesis of efficient noble metal-free catalysts remain a challenge.111 Recently, carbon nanomaterials doped with heteroatoms such
as B, N, P, and S have attracted extensive attention due to their excellent electrocatalytic performance for OER and ORR. The modified electroneutrality and charge modulation induced by heteroatoms have led to enhanced electrocatalytic activity. For example, Qu et al. prepared nitrogen-doped graphene by chemical vapor deposition (CVD) that shows excellent ORR activity. Hu et al. demonstrated ORR, OER and HER activity from N and S co-doped graphitic sheets. Lu et al. reported the enhanced OER performance from multiwall carbon nanotubes treated by surface oxidation, hydrothermal annealing and electrochemical activation. Although the metal-free catalysts have proven to be promising candidates for electrocatalysis, the complicated and multi-step synthetic process requiring CVD and hydrothermal reactions is a disadvantage for large-scale applications. The facile synthesis of catalysts with excellent electrocatalytic performance and understandable mechanistic behaviors remain of interest.

We present here an efficient metal-free catalyst for OER/ORR based on oxidized laser-induced graphene (LIG-O). LIG is a 3D porous graphene material fused to a flexible substrate that is prepared by a one-step laser scribing process on commercial polyimide (PI, Kapton®) film. LIG derived from PI is highly porous and is easily formed in the air at room temperature in a scalable process. The oxidation of LIG by an O₂ plasma to form LIG-O boosted its OER performance, exhibiting a low onset potential of 260 mV with a low Tafel slope of 49 mV dec⁻¹, as well as an increased activity for ORR. Additionally, LIG-O showed unexpectedly high activity in catalyzing Li₂O₂ decomposition in Li-O₂ batteries. The overpotential upon
charging was decreased from 1.01 V in LIG to 0.63 V in LIG-O. The oxygen-containing groups make essential contributions, not only by providing the active sites, but also by facilitating the adsorption of OER intermediates and lowering the activation energy. LIG-O and other oxidized graphitic nanomaterials may be promising catalysts for various energy related applications.

3.2. Oxidized Laser-Induced Graphene for Efficient Oxygen Electro catalysis

3.2.1. Experimental Section

3.2.1.1. Material Synthesis

Preparation of laser-induced graphene (LIG). All samples were prepared under room temperature and ambient air. Kapton® PI films (McMaster-Carr, Cat. No. 2271K3, thickness: 0.005”) were used as received. LIG was generated by a CO₂ laser cutter system (10.6 µm, Universal XLS10MWH laser cutter platform) on the Kapton® polyimide film in air using 3% of full power and 5% of full speed with an image density of 6.

Preparation of oxidized laser-induced graphene (LIG-O). The incorporation of oxygen functional groups to LIG was performed using a Model 1020 Plasma Cleaner (Fischione Instruments). Briefly, the as-prepared LIG on PI was placed in the plasma cleaner chamber and the oxidation was performed in the O₂ environment for 10 min. Then the LIG-O was scratched from the PI for further testing.
Preparation of thermally annealed (LIG-A). ~10 mg LIG was thermally reduced at 750 °C for 2 h in an Ar atmosphere at a ramping rate of 5 °C min⁻¹. The thermal reduction removed most of the oxygen-containing groups on the LIG.

3.2.1.2. Material Characterization

General characterization. SEM images were obtained on a FEI Quanta 400 high-resolution field emission SEM. TEM images were obtained by a JEOL 2100F field emission gun transmission electron microscope. XPS was done by a PHI Quantera SXM scanning X-ray microprobe with a monochromatic 1486.7 eV Al KR X-ray line source, 45° take off angle, and a 200 µm beam size. Raman spectroscopy was performed at 532 nm laser excitation. ICP-OES was carried using a Perkin Elmer Optima 8300 instrument. The BET characterization was done by a Quantachrome Autosorb-3b BET surface analyzer.

Electrochemical measurements. For preparation of the working electrode, 4 mg of the catalyst and 80 µL of 5 wt% Nafion solution were mixed in 1 mL water/ethanol (1/1, v/v) followed by 2 h bath-sonication (Cole Parmer, model 08849–00) to form a homogeneous ink. 8 µL of the ink was loaded onto a rotating disk electrode (RDE, glassy carbon, 5 mm in diameter), and dried in air at room temperature. RuO₂ (Aldrich Chemical Company, Inc.) working electrode was prepared by the same procedures for comparison. The electrochemical measurements were carried out in a 3-electrode configuration using a CHI 608D electrochemical workstation. A Pt plate and Hg/HgO (1 M KOH) were used as the
counter and reference electrode, respectively. The tests regarding oxygen evolution were done on the RDE at 1600 rpm in 1 M KOH with 95% iR compensation unless otherwise noted. 95% instead of 100% iR compensation was applied to avoid the possible over-compensated resistance during the test, because the equivalent serial resistance might be affected by bubble generation/desorption, turbulence and the local change of pH at high current density. The potential was normalized with RHE. The tests regarding oxygen reduction were done in 0.1 M KOH with 95% iR compensation. O2 bubbling in the electrolyte was maintained throughout the measurement to ensure the continuous saturation of O2.

For the OER test at different temperatures, a Ag/AgCl electrode (with saturated potassium chloride electrolyte) was used as the reference electrode. The test was carried out using RDE at 1600 rpm in 1 M KOH. The effects of temperature on pH and the potential of Ag/AgCl were corrected.

The number of electrons transferred \((n)\) during ORR was calculated by Koutecký-Levich (K-L) equation based on the LSV curves with varying rotating speed from 225 to 1600 rpm. According to Equation 3.1, at various electrode potentials:

\[
\frac{1}{j} = \frac{1}{j_K} + \frac{1}{j_L} = \frac{1}{j_K} + \frac{1}{B\omega^{1/2}}
\]

\[
B = 0.2nFC_0D_0^{2/3}v^{-1/6}
\]

where $j$ is the measured current density, and $j_K$ and $j_L$ are the kinetic and diffusion-limiting current densities, respectively. $\omega$ is the rotating speed in rpm, $F$ is the Faraday constant (96485 C mol$^{-1}$), $C_0$ is the bulk concentration of O$_2$ ($1.2 \times 10^{-6}$ mol cm$^{-3}$), $D_0$ is the diffusion coefficient of O$_2$ in 0.1 M KOH ($1.9 \times 10^{-5}$ cm$^2$ s$^{-1}$), and $\nu$ is the kinematic viscosity of the electrolyte (0.01 cm$^2$ s$^{-1}$).

Rotating ring-disk electrode (RRDE) measurement. The catalyst inks and electrodes were prepared by the same method as those of RDE. We combined a CHI 608D workstation (CH Instruments, Inc.) with a CV-50W Voltammetric Analyzer (Artisan) to carry out the measurement. The disk electrode was scanned at a rate of 20 mV s$^{-1}$ and the ring potential was kept constant at 0.4 V vs. Ag/AgCl. The HO$_2^-$ yield and $n$ were calculated using Equation 3.2 and Equation 3.3:

$$\text{HO}_2^-\% = 200\% \times \frac{I_r/N}{I_r/N + I_d}$$

Equation 3.2. Calculation of the HO$_2^-$% from the RRDE measurement.

$$n = 4 \times \frac{I_d}{I_r/N + I_d}$$

Equation 3.3. Calculation of $n$ from the RRDE measurement.

where $I_d$ is disk current, $I_r$ is ring current and $N$ is collection efficiency (0.38).
3.2.1.3. DFT Calculation

The structural optimizations were carried out by adopting the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, along with the projector-augmented wave (PAW) potentials. The electronic wave functions were expanded in a plane wave basis set with the kinetic energy cutoff of 400 eV. For the Brillouin zone integration, $2 \times 1 \times 1$ Monkhorst-Pack k-point meshes were used. The energy convergence criterion for the electronic wavefunction was set to be $10^{-5}$ eV. A vacuum distance of about 10 Å was chosen to guarantee a negligible spurious interaction between layers.

As has been proposed, the free energy of O$_2$ is derived as $G(O_2) = 2G(H_2O) - 2G(H_2) + 4.92$ eV, where 4.92 eV is taken from the free energy change of reaction $O_2 + 2H_2 \rightarrow 2H_2O$ under the standard condition. The free energy of OH$^-$ is determined as $G(OH^-) = G(H_2O) - G(H^+)$ assuming $H^+ + OH^- \rightarrow H_2O$ is in equilibrium. The free energy of H$, G(H^+)$, is that of half of hydrogen molecule, $1/2G(H_2)$. At a pH different from 0, $G(H^+)$ is corrected by the concentration dependence of the entropy, $G(pH) = kT\ln[H^+] = -kT\ln10 \times pH$. The effect of the bias is included for all states involving electrons in the electrode, by shifting the energy of this state by $-neU$, where $n$ and $U$ are the number of electrons involved and the electrode potential, respectively. Under these approximations, the maximum potential achieved by thermodynamics is $\sim 0.4$ eV at pH = 14, which is consistent with the standard reduction potential of the OER in alkaline solution. The Gibbs free energies of intermediates at $U = 0$ V is determined as $\Delta G = \Delta E + \Delta ZPE - T\Delta S$, where $\Delta E$, $\Delta ZPE$ and $\Delta S$ are the difference in total DFT energies,
zero-point energies due to reactions, and the change of the entropy. \( \Delta E \) are taken from DFT calculations, \( \Delta ZPE \) and \( \Delta S \) are taken from references.\textsuperscript{123,124}

### 3.2.1.4. Electrochemically active surface area and electrochemical impedance spectroscopy

The electrochemically active surface area (EASA) is calculated from the double-layer capacitance of the catalyst.\textsuperscript{79} Typically, the CV curves of LIG catalysts were recorded in non-Faradic region (-0.05 to 0.05 V vs Hg/HgO in 1 M KOH) at scan rates ranging from 10 to 100 mV s\(^{-1}\). The current density \( j \) solely originated from the charging/discharging of the double layer capacitance as given by:

\[
 j = C_{dl} \cdot \frac{dV}{dt}
\]

**Equation 3.4. Calculation of the \( C_{dl} \) of LIG-based catalysts.**

\[
\text{EASA} = \frac{C_{dl}}{C_s}
\]

**Equation 3.5. Calculation of the EASA of LIG-based catalysts.**

where \( C_s \) is the ideal specific capacitance of a smooth planar surface. The value of \( C_s \) is determined to be 40 \( \mu \)F cm\(^{-2}\) according to a recent study, where the \( C_s \) values on a variety of electrodes have been evaluated in 1 M OH.\textsuperscript{79} 40 \( \mu \)F cm\(^{-2}\) is a creditable value according to the results from a variety of electrode surfaces.\textsuperscript{79} The geometric
surface area (GSA) of the glassy carbon electrode is 0.196 cm$^2$. The $j$ is recorded at 0 V (vs Hg/HgO).

The electrochemical impedance spectroscopy (EIS) measurements were performed by a CHI 608D electrochemical workstation. EIS spectra were collected by applying ac potentials covering the frequency range from 100000 to 0.1 Hz with an amplitude of 5 mV. Nyquist plots were used to study the surface intermediates coverage and charge transfer properties of the electrodes. The equivalent circuit used to simulate the electrochemical process is shown in Figure 3.1.125

![Figure 3.1. Equivalent circuit for the EIS analysis of LIG-based catalysts.](image)

$R_s$ is the equivalent series resistance and $C_{dl}$ is double-layer capacitance. $R_1 + R_2$ represents the charge transfer resistance. $C_{ads}$ is the capacitance associated with the intermediate adsorbed on the electrode during oxygen evolution. The relation between $C_{ads}$ and the surface coverage ($\theta$) of intermediate at a potential is defined as in Equation 3.6.126

$$C_{ads}(E) = \sigma \frac{d\theta(E)}{dE}$$
Equation 3.6. Determination of the $C_{ads}$.

$\sigma$ is the charge density for a monolayer coverage and is assumed to be constant. $C_{ads}$ is obtained from the EIS and normalized by EASA. The surface coverage is estimated by integrating $C_{ads}$ with $E$, and normalized at a potential below OER onset (1.21 V vs RHE).

3.2.1.5. Identification of the OER rate determining step (RDS)

The OER mechanistic pathways on carbon-based catalysts are generally considered as in the following Equation 3.7.127

\[
\begin{align*}
M + OH^- &\rightarrow M - OH^* + e^- \cdots (a) \\
M - OH^* + OH^- &\rightarrow M - O^* + e^- \cdots (b) \\
M - O^* + OH^- &\rightarrow M - OOH^* + e^- \cdots (c) \\
M - OOH^* + OH^- &\rightarrow M + H_2O + O_2 + e^- \cdots (d)
\end{align*}
\]

Equation 3.7. Proposed OER mechanistic pathways.

M is a catalytically active surface site, and the superscript * means it is a surface state.
Since the LSV curves were recorded at a very low scan rate, only the RDS would be irreversible while all other elementary steps were in quasi-equilibrium. The total anodic current is limited by the RDS and expressed by Equation 3.8.\textsuperscript{128}

\[ i = i_0 e^{\alpha_a F \eta / RT} \]

**Equation 3.8. Effect of overpotential on the anodic current.**

where \( i_0 \) is the exchange current, \( \alpha_a \) is the transfer coefficient, \( F \) is Faraday’s constant and \( \eta \) is the overpotential. Then the Tafel slope \( b \) is determined by Equation 3.9.

\[ b = \frac{\partial \eta}{\partial \log i} = 2.303 \frac{RT}{\alpha_a F} \]

**Equation 3.9. Relationship between Tafel slope and transfer coefficient.**

For a multistep reaction that has one RDS, the \( \alpha_a \) can be estimated by Equation 3.10.\textsuperscript{128}

\[ \alpha_a = \frac{n_f}{\nu} + n_r \beta \]

**Equation 3.10. Estimation of the transfer coefficient in OER.**

where \( n_f \) is the number of electrons transferred before RDS, \( \nu \) is the number of times that RDS occurs, \( n_r \) is the number of electrons transferred in RDS. \( \beta \) is the
symmetry factor, and indicates how the changes in overpotential will affect the changes in the activation energy. $\beta$ is generally assumed to be 0.5.$^{129}$

For a preliminary estimation, if Equation 3.7a is the RDS, $n$ is 0, $n_r$ is 1 and $\alpha_a$ is 0.5. The Tafel slope $b$ would be $\sim 120$ mV dec$^{-1}$. If Equation 3.7b is the RDS, $n$ is 1, $\nu$ is 1, $n_r$ is 1 and $\alpha_a$ is 1.5. The Tafel slope $b$ would be $\sim 40$ mV dec$^{-1}$. Hence, based on the electrochemiucal data (see below), for LIG-O, Equation 3.7b is the RDS. For LIG-A, Equation 3.7a is the RDS.

The surface coverage $\theta$ is further included to study the reaction mechanism.$^{125,126}$ For LIG-A, Equation 3.7a is the RDS and thus the current is related to the velocity $\nu$ of the RDS as shown by Equation 3.11:$^{129}$

$$i \propto \nu = k_1 \cdot \theta_M \cdot a_{OH^-} \cdot e^{\frac{\beta FE}{RT}}$$

Equation 3.11. Effect of overpotential on the anodic current of LIG-A.

$k_1$ is forward rate constant and $E$ is the applied potential. $\theta_M$ is the proportion of surface sites exist as M. Its value ranges from 0 to 1, suggesting no M or all the sites exist as M. It is not applicable to normalize the surface coverage $\theta$ to unity. But it is reasonable that $\theta$ will increase as the potential increases. For LIG-A at low overpotential ($\eta = 300-400$ mV) where the OER starts to happen, $\theta_M$ is close to 1. Hence, the Tafel slope is shown as Equation 3.12:

$$b_{\text{LIG-A}} = \frac{\partial \eta}{\partial \log i} = \frac{\partial E}{\partial \log \nu} = 2.303 \frac{RT}{\beta F} = \sim 120 \text{ mV dec}^{-1}$$

The observed \( b \) of LIG-A is 117 mV dec\(^{-1}\) (see below) that agrees with the analysis.\(^{129}\)

For LIG-O, **Equation 3.7b** is the RDS and the current is related to the velocity of the RDS in **Equation 3.13**:\(^{129}\)

\[
i \propto \nu = \theta_{M-OH} \cdot a_{OH^-} \cdot e^{\frac{\beta FE}{RT}}
\]

**Equation 3.13. Effect of overpotential on the anodic current of LIG-O.**

In this case, **Equation 3.7a** is in equilibrium as show as **Equation 3.14**:

\[
k_1 \cdot \theta_M \cdot a_{OH^-} \cdot e^{\frac{\beta FE}{RT}} = k_{-1} \cdot \theta_{M-OH} \cdot e^{\frac{(\beta-1)FE}{RT}}
\]

**Equation 3.14. OER equilibrium reaction of LIG-O.**

Therefore:

\[
\nu = \theta_{M-OH} \cdot a_{OH^-} \cdot e^{\frac{\beta FE}{RT}} = \theta_M \cdot \frac{k_1}{k_{-1}} \cdot a_{OH^-}^2 \cdot e^{\frac{(\beta+1)FE}{RT}}
\]

**Equation 3.15. Estimation of the reaction velocity for LIG-O.**

And the Tafel slope is shown as **Equation 3.16**:
\[ b_{\text{LIG-O}} = \frac{\partial E}{\partial \log \upsilon} = 2.303 \frac{RT}{(\beta + 1)F} = \sim 40 \text{ mV dec}^{-1} \]

**Equation 3.16. Estimation of the Tafel slope for LIG-O.**

It should be noted that, as the overpotential is increased, the \( \Delta G \) of Equation 3.7a will be further lower (more negative) and the formation of M-OH\(^*\) is preferred at high overpotential. As a result, at higher overpotential \( \theta_{\text{M-OH}} \) will be close to 1, and the Tafel slope is shown as **Equation 3.17:**

\[ b = \frac{\partial E}{\partial \log \upsilon} = 2.303 \frac{RT}{\beta F} = \sim 120 \text{ mV dec}^{-1} \]

**Equation 3.17. Estimation of the Tafel slope for LIG-O at high overpotential.**

The experimental data (see below) shows the two Tafel regions with \( b \) of 49 and 134 mV dec\(^{-1}\), demonstrating the proposed mechanism of LIG-O. It should be noted that in practical measurements (especially at high overpotential), experimental factors such as mass transport limitations, charge transfer efficiency, side reactions at high potential etc. will have interference on the Tafel plots, and lead to a much higher \( b \).

Our analysis has shown the two distinct RDS of LIG-O and LIG-A based on the surface coverage \( \theta \) and overpotential \( \eta \). The RDS of LIG-A is the formation of discrete adsorbed hydroxide intermediates which may be ascribed to the low content of oxygen-containing groups. The RDS of LIG-O is the formation of epoxide on the
surface of LIG. The low affinity (compared with transition metal oxides) may be rate-determining.

3.2.1.6. Li-O₂ battery using LIG as the air cathode

Briefly, a piece of LIG-O film was carefully scraped from the PI substrate and used as the air cathode without any binders or catalysts. The cells were assembled in an argon-filled glovebox with a lithium metal anode. The separator was Celgard 2400 membrane. A stainless-steel mesh was used as the supporter and current collector for the LIG-O film to allow O₂ diffusion. The electrolyte was 0.5 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) with 0.05 M LiI in tetraethylene glycol dimethyl ether (TEGDME). The total area of the cathode that exposed to O₂ was 12.5 mm² (0.063 mg of LIG-O). Li-O₂ batteries with commercially available Pt/C (Sigma-aldrich, 205931) as the cathode catalysts were fabricated for comparison. Then the cells were rested at open circuit condition with O₂ purging for 10 h prior to test. For the galvanostatic charge/discharge measurements, the current was kept constant at 0.01 mA and the time was limited to 6h. The lower and upper voltage limits were 2.5 and 4.3 V (vs Li), respectively.

3.2.2. Result and Discussion

As depicted in Figure 3.2a, the LIG-O was prepared by direct laser scribing on Kapton® PI films followed by O₂ plasma treatment, which is known to create surface defects and oxygen-containing groups on carbon materials. According to previous work on graphene, the LIG powder (removed from the PI substrate) was heated at
750 °C in Ar for 2 h to remove most of the surface oxygen-containing groups to produce annealed LIG (LIG-A).\textsuperscript{132,133} The highly porous filiform structure of LIG was maintained in LIG-O after the O\textsubscript{2} plasma treatment as shown in the scanning electron microscope (SEM) images in Figure 3.2b, Figure 3.3 and Figure 3.4. However, this structure collapsed slightly after thermal annealing and resulted in the flake-like structure of LIG-A as shown in Figure 3.5. The typical multilayer graphitic structure of LIG remained after either treatment, as revealed by the transmission electron microscopy (TEM) images in Figure 3.2, Figure 3.6 and Figure 3.7, which is consistent with the clearly identified D, G and 2D peaks in the Raman spectra (Figure 3.8).\textsuperscript{28} LIG-O has abundant graphene edge structures that improve the electrolyte wettability and retain good electric conductivity. The \( I_D/I_G \) increased after the treatments, indicating that more defects were formed.\textsuperscript{134} Oxygen plasma treatment also increased the porosity of LIG. The Brunauer-Emmett-Teller (BET) surface area of LIG-O is 246.8 m\(^2\) g\(^{-1}\), whereas that of LIG is 178.7 m\(^2\) g\(^{-1}\) (Figure 3.8).
Figure 3.2. Preparation and structural characterization of LIG-O. (a) Preparation of LIG-O. (b) SEM and (c) TEM images of LIG-O.
Figure 3.3. SEM images of LIG-O.

Figure 3.4. SEM images of LIG.

Figure 3.5. SEM images of LIG-A.
Figure 3.6. TEM images of LIG-O.
Figure 3.7. TEM images of LIG-A.

Figure 3.8. Raman spectra and BET measurement. (a) Raman spectra of LIG-O, LIG and LIG-A. (b) The ratio between the intensities of D and G band in (a). And nitrogen adsorption/desorption plot of (c) LIG and (d) LIG-O.

The OER activities of LIG-O, LIG and LIG-A were characterized in 1 KOH by using a rotating disk electrode (RDE, glassy carbon (GC)) loaded with the catalyst ink at 1600 rpm, with a Pt counter electrode and a Hg/HgO reference electrode. The use of RDE was to ensure electrolyte mixing and fast removal of bubbles generated at the catalyst surface. As shown by the linear sweep voltammetry (LSV) results in Figure...
3.9a, LIG was moderately active for OER while LIG-O showed a remarkably lowered onset potential of 260 mV with enhanced current density ($j_{GSA}$, current normalized by the geometric surface area of the electrode). The $j_{GSA}$ of LIG-O reached 10 mA cm$^{-2}$ at a low overpotential of 364 mV; such a low value is comparable to that of transition metal-based catalysts.$^{79, 135-138}$ Figure 3.9b shows the Tafel plots derived from the LSV curves. The Tafel slope of LIG-O is 49 mV dec$^{-1}$, which is lower than most metal-free catalysts (Table 3.1), demonstrating the significantly enhanced OER activity after O$_2$ plasma treatment. LIG-A has a performance inferior to LIG-O and LIG, with an onset potential of 290 mV and a Tafel slope of 117 mV dec$^{-1}$. Although the benchmark RuO$_2$ has the lowest onset potential of 210 mV, the higher Tafel slope of 67 mV dec$^{-1}$ made its performance less competitive with LIG-O at high current density. The Tafel slope of RuO$_2$ ranges from $\sim$50 to $\sim$100 mV dec$^{-1}$ in the literature, probably due to the structurally sensitive activity on RuO$_2$ in that the Tafel slope depends on the orientation of the lattice.$^{135, 136}$ LIG-O also showed impressive OER activity in 0.1 M KOH (Figure 3.10). The onset potential was 290 mV with a Tafel slope of 56 mV dec$^{-1}$ and the overall performance surpassed that of RuO$_2$. 
Figure 3.9. OER performance characterized in 1 M KOH.
(a) LSV curves of LIG-O, LIG, LIG-A and a GC electrode recorded in 1 M KOH at a scan rate of 2 mV s⁻¹. (b) Tafel plots calculated from (a). (c) LSV curves with current normalized by the EASA. (d) Stability test. Potential profile of LIG-O for bulk OER at 5 mA cm⁻².
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Onset potential (V)</th>
<th>Tafel Slope (mV dec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIG-O</td>
<td>1 M KOH</td>
<td>1.49</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>0.1 M KOH</td>
<td>1.52</td>
<td>56</td>
</tr>
<tr>
<td>N, O, P tri-doped porous carbon⁴³⁹</td>
<td>1 M KOH</td>
<td>1.52</td>
<td>84</td>
</tr>
<tr>
<td>O-CNTs⁴⁰</td>
<td>1 M KOH</td>
<td>1.52</td>
<td>47.7</td>
</tr>
<tr>
<td>Pristine CNTs⁴¹</td>
<td>1 M KOH</td>
<td>1.58</td>
<td>60</td>
</tr>
<tr>
<td>B doped CNTs⁴²</td>
<td>1 M KOH</td>
<td>1.65</td>
<td>/</td>
</tr>
<tr>
<td>NG-CNT⁴³</td>
<td>0.1 M KOH</td>
<td>1.54</td>
<td>141</td>
</tr>
<tr>
<td>N, S co-doped graphitic sheets⁴²⁰</td>
<td>0.1 M KOH</td>
<td>1.49</td>
<td>71</td>
</tr>
<tr>
<td>N, S co-doped Graphene⁴⁴⁴</td>
<td>0.1 M KOH</td>
<td>1.52</td>
<td>59</td>
</tr>
<tr>
<td>Oxidized carbon cloth⁴⁵⁴</td>
<td>0.1 M KOH</td>
<td>1.56</td>
<td>82</td>
</tr>
<tr>
<td>O-Graphene Foam⁴⁶</td>
<td>0.1 M KOH</td>
<td>1.57</td>
<td>137</td>
</tr>
</tbody>
</table>

Table 3.1. Comparison of OER performance of LIG-O with recently reported metal-free OER catalysts.
The OER activities were further studied based on the electrochemically active surface area (EASA) that was calculated from the double-layer capacitance recorded in the non-Faradic region (Experimental Section and Figure 3.11).\textsuperscript{79} LIG-O has the highest EASA of 83.6 cm\textsuperscript{2} per geometric cm\textsuperscript{2} of the GC electrode. The values of LIG and LIG-A are 36.3 and 33.0 cm\textsuperscript{2}, respectively. The high EASA of LIG-O indicates its porous structure and good compatibility with the electrolyte. It should be noted that the increased hydrophilicity after oxidation may have also contributed to the high EASA. As shown in Figure 3.9c, LIG-O has a much higher $j_{\text{EASA}}$ than that of LIG and LIG-A, indicating that the oxidation not only increased the EASA of LIG, but also created more active sites; both contributed to the high activity. At 350 mV overpotential, the $j_{\text{EASA}}$ of LIG-O is as high as 0.08 mA cm\textsuperscript{2}; this value is higher than that of transition metal based catalysts.\textsuperscript{121} Additionally, the long-term stability of LIG-O is outstanding as
shown in Figure 3.9d. After bulk OER at 5 mA cm$^{-2}$ for 20000 s, the overpotential slightly increased by 13 mV, suggesting a negligible degradation of the catalysts.

Figure 3.11. Determination of the $C_{dl}$ and EASA.
CV curves recorded at 10, 20, 40, 60, 80 and 100 mV s\(^{-1}\) for (a) LIG-O, (c) LIG and (e) LIG-A. Current density at 0 V (vs Hg/HgO) as a function of scan rate for (b) LIG-O, (d) LIG and (f) LIG-A. The contact angle measurements and wettability of surfaces of (g) LIG and (h) LIG-O on PI substrate.

In order to explain the high OER activity of LIG-O, we first excluded the contamination by metal impurities. The CV curve (Figure 3.12) shows no redox peaks in the OER region, indicating that the OER activity was not from any redox mediator (e.g. Ni\(^{2+} \rightarrow \) NiOOH). Likewise, no nanoparticles were observed in the TEM images. This is consistent with the high-resolution XPS spectra shown in Figure 3.13, where no detectable contamination of Ni, Co or Fe was found (the transition metal oxides are generally considered highly active for OER). Inductively coupled plasma optical emission spectrometry (ICP-OES) confirmed there is no detectable contamination from Co, Ni or Fe species (<0.0005 at%).

Figure 3.12. CV curve of LIG-O in 1 M KOH.
Figure 3.13. XPS spectra of LIG-O. (a) XPS survey spectrum of LIG-O. Elemental spectra in (b) Fe 2p, (c) Co 2p and (d) Ni 2p regions.

Detailed investigations of the OER activity of LIG-O were then carried out. Figure 3.14a shows the elemental composition of the catalysts as determined by XPS, where LIG-O has a high oxygen content of 11.6 % compared to 3.1 % for LIG and 1.4 % for LIG-A (Table 3.2), suggesting the significant effects of oxygen-containing groups on OER activity. High-resolution XPS spectra (Figure 3.14b and Figure 3.14c, Figure 3.15 and Figure 3.16) further reveal the ratios of the oxygen and carbon species. The
O 1s spectra was deconvoluted into three peaks that were assigned to C-O (~533.5 eV), C=O (~532.3 eV) and physisorbed oxygen/carbonate species (~530.5 eV), respectively. The C 1s spectra were deconvoluted into the peaks from sp² (284.5 eV), sp³ (285.0 eV), C-O (285.9 eV), C=O (287.2 eV) and O-C=O (288.7 eV).

As summarized in Table 3.3, LIG-O has the highest C=O content (11.0 % vs 4.8 and 0.2 % of LIG and LIG-A, respectively) while its C-O content is comparable to those of LIG and LIG-A. Hence, the OER activity is strongly correlated to the C=O content. Recent studies on carbon nanotubes suggest that the carbon atoms near C=O are the predominantly active sites for OER due to the charge redistribution induced by the highly electronegative oxygen atoms, a conclusion that is supported by the low activity of LIG-A compared to LIG-O.
Figure 3.14. Analysis on the OER mechanism of LIG-O. (a) XPS survey spectra of LIG-O, LIG and LIG-A. (b) XPS O 1s and (c) C 1s spectra of LIG-O. (d) Surface coverage of OER intermediates. (e) LSV curves of LIG-O recorded at different temperature and (f) Arrhenius plots fitted at different overpotentials.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>C (at%)</th>
<th>O (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIG-O</td>
<td>88.4</td>
<td>11.6</td>
</tr>
<tr>
<td>LIG</td>
<td>96.9</td>
<td>3.1</td>
</tr>
<tr>
<td>LIG-A</td>
<td>98.6</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table 3.2. Elemental composition of LIG-O, LIG and LIG-A from XPS.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>sp²</th>
<th>sp³</th>
<th>C-O</th>
<th>C=O</th>
<th>O-C=O</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIG-O</td>
<td>60.3</td>
<td>20.6</td>
<td>7.0</td>
<td>11.0</td>
<td>3.1</td>
</tr>
<tr>
<td>LIG</td>
<td>65.7</td>
<td>24.2</td>
<td>5.3</td>
<td>4.8</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>LIG-A</td>
<td>66.7</td>
<td>28.1</td>
<td>4.1</td>
<td>0.2</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

Table 3.3. XPS fitting results of carbon species on LIG-O, LIG and LIG-A (at%).
First-principles calculations were exploited to understand and quantify the mechanism of OER catalysis at graphene edges.\textsuperscript{152, 153} The spin-polarized density
functional theory (DFT) calculations were performed using the Vienna \textit{ab-initio} simulation package (VASP)\textsuperscript{152, 153} code (Experimental Section). As shown in \textbf{Figure 3.17} and \textbf{Figure 3.18}, the edge sites on graphene that are adjacent to C=O were taken into consideration to determine the change of Gibbs free energy which represents the thermodynamic barriers during OER. In the 4-electron OER process, the step with maximum Gibbs free energy change ($\Delta G_{\text{max}}$) is recognized as the thermodynamics-limiting step as shown in \textbf{Figure 3.17}e. The for the oxygen-free edges, the $\Delta G_{\text{max}}$ are higher than 1.27 eV (\textbf{Table 3.4}), which indicates a very high overpotential for OER. On the contrary, a low $\Delta G_{\text{max}}$ of 0.49 eV was found for the oxygen-containing edges (hex-O-C). The LIG-O has abundant edges as revealed by the TEM and EASA analyses, and thus has more active sites in good contact with the electrolyte. The C=O moieties on or near the five/seven-membered rings may also activate their neighboring carbon atoms to have higher OER activity, since the distorted electron clouds around the five/seven-membered rings would be more easily affected. An abundance of five/seven-membered rings are present in LIG since it forms through a rapid cooling in the lasing process, making it kinetic graphene-like.\textsuperscript{28} For instance, the $\Delta G_{\text{max}}$ of a pentagonal site is 0.72 eV and thus these sites may be catalyzing OER as the overpotential increases (pen-O-C in \textbf{Figure 3.17}). These calculations show that the oxygen-defects may indeed significantly enhance the OER performance of graphene edges by lowering the $\Delta G_{\text{max}}$ on adjacent carbons.
Figure 3.17. DFT simulation results of LIG-based catalyst. Atomic structures and nonequivalent sites at graphene edges with (a) oxygen adsorbed hexagon marked as hex-O-A, -B, -C, -D, (b) oxygen adsorbed pentagon as pen-O-A, -B, -C, (c) hexagon as hex-A, -B, (d) pentagon as pen-A, -B. Gray and red balls represent carbon and oxygen atoms, respectively. (e) Gibbs free energy diagrams for OER on nonequivalent graphene edge sites in alkaline solution under conditions of pH 14 and the maximum potential allowed by thermodynamics. Figure credit to Luqing Wang and Prof. Yakobson.
Figure 3.18. OER intermediates adsorption structures on edge sites. 
(a) oxygen adsorbed hexagon marked as hex-O-A, -B, -C, -D, (b) oxygen adsorbed pentagon as pen-O-A, -B, -C and (c) hexagon as hex-A, -B and pentagon as pen-A, -B. Gray and red balls represent the carbon and oxygen atoms, respectively. Figure credit to Luqing Wang and Prof. Yakobson.
<table>
<thead>
<tr>
<th>sites</th>
<th>$\Delta G_{\text{max}}$ (eV)</th>
<th>sites</th>
<th>$\Delta G_{\text{max}}$ (eV)</th>
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<tr>
<td>hex-A</td>
<td>1.55</td>
<td>pen-A</td>
<td>2.59</td>
</tr>
<tr>
<td>hex-B</td>
<td>1.32</td>
<td>pen-B</td>
<td>1.27</td>
</tr>
<tr>
<td>hex-O-A</td>
<td>2.66</td>
<td>pen-O-A</td>
<td>1.52</td>
</tr>
<tr>
<td>hex-O-B</td>
<td>1.42</td>
<td>pen-O-B</td>
<td>1.42</td>
</tr>
<tr>
<td>hex-O-C</td>
<td>0.49</td>
<td>pen-O-C</td>
<td>0.72</td>
</tr>
<tr>
<td>hex-O-D</td>
<td>1.78</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.4. OER catalytic sites at graphene edges and the corresponding $\Delta G_{\text{max}}$.

In addition to the thermodynamic analysis, we focused on the reaction kinetics of LIG-O since the reaction is energetically favorable at potentials beyond the onset. The generally considered four-electron oxidation pathway for OER in alkaline is shown in Equation 3.7 (Experimental Section):\textsuperscript{127,154}

\[
\begin{align*}
M + \text{OH}^{-} & \rightarrow M - \text{OH}^* + e^- \cdots (a) \\
M - \text{OH}^* + \text{OH}^{-} & \rightarrow M - \text{O}^* + e^- \cdots (b) \\
M - \text{O}^* + \text{OH}^{-} & \rightarrow M - \text{OOH}^* + e^- \cdots (c)
\end{align*}
\]
\[
\text{M} - \text{OOH}^* + \text{OH}^- \rightarrow \text{M} + \text{H}_2\text{O} + \text{O}_2 + e^- \cdots (d)
\]

**Equation 3.7. Proposed OER mechanistic pathways.**

where \(M\) is the active site and the star (*) means it is a surface state. The Tafel slope analysis (Experimental Section) demonstrates that **Equation 3.7a** is the rate determining step (RDS) for LIG-A whereas **Equation 3.7b** is the RDS for LIG-O. This result is intuitively understandable and further confirmed by the electrochemical chemical impedance\(^{125}\) (Experimental Section) and the estimation of the adsorption of OER intermediates (**Figure 3.14d**).\(^{126}\) As shown in **Figure 3.19**, the charge transfer resistance (\(R_{\text{CT}}\)) of LIG-O greatly decreased from more than 10000 \(\Omega\) to \(~10\ \Omega\) as the potential exceeded the onset potential, suggesting the efficient charge transfer between the electrode and the electrolyte. Conversely, the \(R_{\text{CT}}\) of LIG-A remained as high as 1000 \(\Omega\) even at a higher potential of 1.65 V. The OER intermediate surface coverage (\(\theta\)) was calculated from the capacitance of the intermediate adsorption (\(C_{\text{ads}}\)).\(^{126}\) Since the \(C_{\text{ads}}\) was normalized by EASA, the result shows the intrinsic ability of LIG-O and LIG-A for adsorbing the intermediates. **Figure 3.20** shows the \(C_{\text{ads}}\) at different potentials where LIG-O had much higher \(C_{\text{ads}}\) than LIG-A, especially at the potentials beyond the OER onset. We further calculated the \(\theta\) by integrating the \(C_{\text{ads}}\) with potential as in **Equation 3.6**(Experimental Section):\(^{126, 140}\)

\[
C_{\text{ads}}(E) = \sigma \frac{d\theta(E)}{dE}
\]

**Equation 3.6. Determination of the \(C_{\text{ads}}\).**
where \( \sigma \) is the charge density for a monolayer coverage and is assumed to be constant and the same for LiG-O and LiG-A. LiG-O has much higher \( \theta \) value than LiG-A, which is consistent with the OER activity. As for LiG-A, the low C=O content not only limited the number of active sites, but also hindered the first OER step (Equation 3.7a) resulting in a high Tafel slope of 117 mV dec\(^{-1}\), while LiG-O benefited from the high C=O content, and the Tafel slope is as low as 49 mV dec\(^{-1}\) (Figure 3.21). Furthermore, we estimated the apparent activation energy (\( E_{\text{app}} \)) of the RDS assuming that the velocity of OER was solely dominated by the RDS\(^{155, 156} \). The data are summarized in Figure 3.14 and Figure 3.22 where \( E_{\text{app}} \) was extracted from the Arrhenius plots. Increasing the temperature slightly increased the current density of both LiG-O and LiG-A. However, the \( E_{\text{app}} \) of LiG-A was \(~15\) kJ mol\(^{-1}\) higher than that of LiG-O. The effect of overpotential on the \( E_{\text{app}} \) was further deduced (assuming the symmetry factor \( \beta = 0.5 \) and the RDS is not thermodynamically limited) to yield the intrinsic activation energy (\( E_{\text{int}} \)) as shown in Figure 3.22\(^{129} \). The \( E_{\text{int}} \) of LiG-O is significantly lower than that of LiG-A by \(~20\) kJ mol\(^{-1}\), indicating that the velocity of the RDS of LiG-O is \(~3000\) times higher than that of LiG-A under the same overpotential at room temperature. As has been discussed, the carbon atoms near C=O are the predominate active sites for OER, thus the concentration of C=O also has significant effect on the OER reaction kinetics not only by inducing the active sites, but also by facilitating the adsorption of OER intermediates and lowering the activation energy.
Figure 3.19. EIS analysis of LIG-O and LIG-A. Nyquist plots of (a) LIG-O and (b) LIG-A. The fitted $R_{CT}$ and $R_s$ of (c) LIG-O and (d) LIG-A at different potentials.
Figure 3.20. $C_{ads}$ (normalized by EASA, $\mu$F cm$^{-2}$) of LIG-O and LIG-A.

Figure 3.21. Tafel slope of LIG-O at different overpotentials.
Figure 3.22. OER reaction kinetics of LIG-O and LIG-A. (a) LSV curves of LIG-A recorded at different temperature and (b) Arrhenius plots fitted at different overpotentials; the activation energy fitting results for (c) LIG-A and (d) LIG-O.

The oxidation of LIG promoted the OER activity and improved the ORR activity. The ORR performance was characterized by CV in O$_2$-saturated 0.1 M KOH (Figure 3.23). Both the LIG-O and LIG-A showed a reduction peak. The onset potential of LIG-A was 0.68 V with a peak potential at 0.46 V, while the onset and peak potentials of LIG-O were 0.77 and 0.60 V, respectively. The positively shifted potentials indicate the improved ORR performance of LIG-O, which was also evidenced by the increased...
area of the CV curve. The ORR kinetics was investigated using the Koutecký-Levich equation and rotating ring-disk electrodes (RRDE), respectively (Figure 3.23, Figure 3.24 and Figure 3.25). The Tafel slope of LIG-O is as low as 90 mV dec⁻¹. The electron transfer number \( n \) of LIG-O was calculated to be 4.0 at 0.6 V, suggesting an efficient four-electron transfer pathway to generate OH⁻. However, \( n \) decreased to 2.8 as the potential decreased to 0.4 V, indicating the coexistence of a pathway producing \( \text{H}_2\text{O}_2 \). In comparison, LIG-A has a \( n \) of 2.5-2.8 through 0.6 to 0.4 V. The decrease in \( n \) was caused by the two-electron transfer process on the pristine carbon surfaces. This observation suggested that both LIG-O and LIG-A underwent the four-electron transfer pathway while LIG-O showed an enhanced activity. Additionally, the LIG-O has shown good structural stability through the OER and ORR tests.

Figure 3.23. The ORR performance of LIG-O. (a) CV curves of LIG-O and LIG-A recorded in 0.1 M KOH with Ar or \( \text{O}_2 \) bubbling at 50 mV s⁻¹. (b) LSV curves of LIG-O at different rotating speed in 0.1 M KOH with \( \text{O}_2 \) bubbling.
Figure 3.24. Reaction kinetics of the ORR of LIG-O. 
(a) Koutecký-Levich plots and (b) Tafel plots of LIG-O for ORR. (c) Long-term stability of LIG-O for ORR, inset shows the LSV curve at 900 rpm. (d) The RRDE LSV of ORR and (e) the corresponding HO$_2^-$ yield and $n$. 
Figure 3.25. ORR performance of LIG and LIG-A. LSV curves for ORR at different rotation speed and the Koutecký-Levich plots of (a, b) LIG and (c, d) LIG-A, respectively.
Figure 3.26. SEM and Raman characterization of LIG-O after OER and ORR test.

The morphology and graphenic structure were characterized by SEM and Raman, respectively, to reveal the structure of catalysts after OER and ORR test (Figure 3.26). The catalysts were scraped off the GC electrode after electrochemical tests for SEM and Raman characterization. The post-OER and post-ORR LIG-O maintained the porous structure as the pristine LIG-O. Similarly, Raman spectra
shows the characteristic multilayer graphene structure for pristine, post-OER and post-ORR LIG-O. The results showed nearly no significantly change in the structure of the LIG-O, regarding the surface morphology and graphenic structure.

The electrochemical performance of LIG-O in OER and ORR highlighted its potential use in Li-O₂ batteries since a bifunctional material is the prerequisite, especially for the oxygen evolution from the decomposition of Li₂O₂. The electrocatalytic activity of LIG-O was examined in a Li-O₂ battery. The device structure is shown in Figure 3.27a. The CV curves of the battery, which was tested in Ar and O₂ atmosphere at a scan rate of 0.5 mV s⁻¹, are shown in Figure 3.28. The battery showed significantly increased current with redox peaks in O₂ when compared to the results in Ar. The potentials of Li₂O₂ formation and decomposition were 2.76 and 3.49 V, respectively, which are very close to the theoretical potential of 2.96 V, indicating the high activity of the LIG-O cathode. The battery was further characterized by galvanostatic discharge/charge tests as shown in Figure 3.27b. Despite the similar overpotential in the discharge process, LIG-O showed a remarkably lowered overpotential of 0.63 V, which was much lower than the overpotential of 1.01 V from the pristine LIG. Additionally, LIG-O showed cycle stability superior to that of LIG and commercial Pt/C as depicted in Figure 3.29. LIG showed increased overpotential in both the charge and discharge processes as the cycle number increased. The LIG-O had much smaller changes in overpotential through 20 cycles. The decomposition of Li₂O₂ at lower potential is of great importance for improving the roundtrip efficiency of batteries. A demonstration of
the LIG-O Li-O₂ battery is presented in **Figure 3.29d**, where a LED (NTE30105, 2.8 V, 25 mA) was lit by one cell. Due to the high activity of LIG-O, it is probable that the performance of LIG-O could be further improved by optimization for practical utilization.

**Figure 3.27.** Li-O₂ battery using LIG-O as the cathode catalyst.
Figure 3.28. CV curves of the Li-O₂ battery with LIG-O cathode at 0.5 mV s⁻¹.

Figure 3.29. Cycling performance of the Li-O₂ batteries. (a) LIG-O, (b) LIG and (c) Pt/C cathode at a current density of 0.16 A g⁻¹. (d) Illustration of the Li-O₂ battery with LIG-O cathode for lighting a yellow-green LED.

3.2.3. Conclusion

In summary, we prepared oxidized LIG-O as an efficient catalyst for oxygen electrocatalysis. The oxidation of LIG with intrinsic high surface area produces abundant active sites for electrocatalysis, leading to the excellent OER/ORR activity.
Additionally, the LIG-O is particularly advantageous for the Li$_2$O$_2$ decomposition that can dramatically lower the overpotential of the charging process by ~380 mV. The outstanding OER performance of LIG-O is rationalized by the oxygen-containing groups (e.g. C=O) that enhance the adsorption of OER intermediates and facilitate the rate-determining step. Benefiting from its high performance with low cost and facile preparation, LIG-O is a promising alternative to metal-based catalysts for water splitting, metal-air/O$_2$ batteries and many other applications. Our findings lead to a better understanding of the catalytic mechanism of LIG derived materials as well as further improvements in the catalytic activity of surface-oxidized carbon nanomaterials.

3.3. Experimental Contributions

**Jibo Zhang** designed the experiments, prepared the samples, and conducted part of the characterizations including Raman, XPS, ICP-OES, electrochemical measurements and etc. **Muqing Ren** designed part of the experiments and conducted part of the characterizations including SEM, TEM, BET and battery test. **Luqing Wang** conducted the theoretical calculation and analysis. **Yilun Li** helped in SEM and TEM.
Chapter 4

In Situ Synthesis of Efficient Water Oxidation Catalysts in Laser-Induced Graphene

This chapter was entirely copied from reference. 161

4.1. Introduction

Electrically splitting water into H₂ and O₂ offers an attractive method for renewable energy storage.162-164 However, the oxidation half reaction of water splitting, which is known as the oxygen evolution reaction (OER),165-167 is kinetically unfavorable and suffers from high overpotential and energy loss as compared with the reduction half reaction, the hydrogen evolution reaction (HER).168-170 Noble metal oxides such as IrO₂ and RuO₂ have shown outstanding catalytic performance in OER, but the large-scale application is restricted by their high cost and low abundance.109. 171 Alternatively, first-row transition metal oxides and hydroxides have garnered attention for their low cost, high activity and stability in basic solutions. Co-/Ni-/Fe-based OER catalysts have undergone extensive research in the past decade.135, 172, 173
Among the various materials, NiFe-based catalysts (oxides and oxyhydroxides) stand out due to their superior performance, showing low onset potentials, low Tafel slopes and excellent durability.\textsuperscript{174-177} Generally, the NiFe catalysts were synthesized by solution-based methods such as co-precipitation,\textsuperscript{178} solvothermal and hydrothermal reaction\textsuperscript{83,180} and electrodeposition.\textsuperscript{66,181} In a recent work, Müller \textit{et al.} demonstrated an alternative approach using pulsed-laser ablation in liquids to synthesize NiFe layered double hydroxides (LDH) that showed an impressively low overpotential of 260 mV at 10 mA cm\textsuperscript{-2} for OER.\textsuperscript{182,183} However, there are very few reports on the direct solid phase synthesis of efficient OER catalysts. A facile and scalable synthetic route to NiFe catalysts is still in demand.

Recently, our group developed a straightforward method to grow porous graphene by direct laser writing on a polyimide (PI) sheet to produce laser-induced graphene (LIG).\textsuperscript{28,122} We further improved the method to prepare metal oxide nanoparticle/graphene composites from metal-complex containing PI films for the oxygen reduction reaction.\textsuperscript{65} But the tedious procedures to incorporate the metal species in poly(amic acid), the PI precursor, followed by thermal curing and post-annealing, diminished the accessibility for practical applications. We present here a significantly improved strategy for synthesizing metal oxide/graphene hybrid materials as highly efficient catalysts for OER. By pre-forming LIG, then merely adding the proper metal precursors to the existing LIG layer, followed by re-lasing, the nucleation of metal oxide nanoparticles ensured that were uniformly embedded in the LIG. Benefiting from this solid phase synthetic method, we prepared a series of
NiFe oxide/graphene hybrid catalysts (NiFe/LIG) that showed remarkably high OER activity, among which the best catalyst had a remarkably low overpotential of 240 mV at 10 mA cm\(^{-2}\) with a Tafel slope of 32.8 mV dec\(^{-1}\) and excellent stability. Moreover, the method is also applicable for non-LIG/PI substrates such as carbon fiber paper (CFP) to a directly fabricated self-supported catalytic electrode.

In addition to the high OER activity of the NiFe/LIG catalysts, the simplified method presented meets the requirement of roll-to-roll production and could be applied to many metal precursors regardless of their solubility and compatibility with the precursor of PI.\(^{65}\) The composition of nanoparticles is conveniently tunable by altering the precursor for applications in various electrocatalytic reactions such as hydrogen evolution and oxygen reduction.

### 4.2. In Situ Synthesis of Efficient Water Oxidation Catalysts in Laser-Induced Graphene

#### 4.2.1. Experimental Section

##### 4.2.1.1. Material Synthesis

**Preparation of LIG.** Kapton\(^{®}\) PI films (McMaster-Carr, Cat. No. 2271K3, thickness: 0.005") were used as received. LIG was generated by a CO\(_2\) laser cutter system (10.6 μm, Universal XLS10MWH laser cutter platform) on the Kapton\(^{®}\) PI in air using 3% of full power and 5% of full speed with an image density of 6. The LIG was patterned on PI as a 2×2 cm\(^2\) square.
Preparation of the catalysts. 1 M NiSO₄ and 1 M FeCl₃ solutions were prepared with deionized water. Then the mixture solutions with different molar ratios ([Ni²⁺]: [Fe³⁺]) were prepared, and the total concentration of metal cations ([Ni²⁺] + [Fe³⁺]) was kept at 1 M. The as-prepared LIG (2 × 2 cm²) was treated in the UV-ozone cleaner (Boekel Model 135500) for 3 min to ensure the wettability of LIG with aqueous solutions. 80 μL of the solutions were dropped uniformly onto the LIG. The soaked LIG (on PI) was dried in air at room temperature overnight and then vacuum (~120 mm Hg) dried for 3 h. The LIG was lasered again on the same LIG pattern under the same conditions (3% of full power and 5% of full speed with an image density of 6). Then the powder was scratched off from the PI using a spatula and collected for characterization.

Preparation of the NiFe/CFP. A piece of carbon fiber paper (CFP, ~1 × 1 cm², FuelCellStore) was treated by a UV-ozone cleaner (Boekel Model 135500) for 5 min to improve the wettability. Then 80 μL of the precursor solution ([Ni²⁺]: [Fe³⁺], 1:1) was dropped onto the CFP. The CFP was dried in air at room temperature overnight and then transferred into a vacuum chamber (~120 mm Hg) and dried at room temperature for 6 h. The CFP was scribed by the laser beam with 3% of full power, 5% of full speed and an image density of 6. The area of the lasered pattern was 7 × 7 mm².

4.2.1.2. Material Characterization

General characterization. SEM images were obtained on a FEI Quanta 400 high-resolution field emission SEM. TEM images and elemental mapping images were
obtained by a JEOL 2100F field emission gun transmission electron microscope. XPS analysis was done on a PHI Quantera SXM scanning X-ray microprobe with a monochromatic 1486.7 eV Al KR X-ray line source, 45° take off angle, and a 200 μm beam size. The XPS spectra were taken from the as-prepared catalysts on PI. Raman spectroscopy was performed at 532 nm laser excitation. ICP-OES was carried out using a Perkin Elmer Optima 8300 instrument.

**Electrochemical measurements.** For the preparation of the working electrode, 4 mg of the carbon-metal catalyst composite and 80 μL of 5 wt% Nafion solution were mixed with 1 mL water/ethanol (4/1, v/v) followed by 2 h bath-sonication (Cole Parmer, model 08849-00) to form a homogeneous ink. 5 μL of the ink was dropped onto a glassy carbon electrode (3 mm in diameter) and dried in air at room temperature (the catalyst loading is ~0.265 mg cm$^{-2}$). The electrochemical measurements were carried out in a 3-electrode configuration using CHI 608D electrochemical workstation. Pt plate and Hg/HgO (in 1 M KOH) were used as the counter and reference electrode, respectively. The tests regarding oxygen evolution were done in 1 M KOH with 95% iR compensation. The potential was normalized with RHE.

The EASA is calculated from the double-layer capacitance of the catalyst. Typically, the CV curves of LIG catalysts were recorded in the non-Faradic region (-0.05 to 0.05 V vs Hg/HgO in 1 M KOH) at scan rates ranging from 10 mV s$^{-1}$ to 100 mV s$^{-1}$. The geometric current density $j_{GSA}$ solely originates from the
charging/discharging of the double layer capacitance as given by the following 

**Equation 4.1** and **Equation 4.2**:

\[ j = C_{dl} \cdot \frac{dv}{dt} \]

**Equation 4.1. Calculation of the \( C_{dl} \) of NiFe/LIG catalysts.**

EASA is calculated based on:

\[ \text{EASA} = \frac{C_{dl}}{C_s} \]

**Equation 4.2. Calculation of the EASA of NiFe/LIG catalysts.**

where \( C_s \) is the ideal specific capacitance of a smooth planar surface. The geometric surface area (GSA) of the glassy carbon electrode is 0.07 cm\(^2\). The value of \( C_s \) is considered as 40 \( \mu \)F cm\(^2\), and the \( j \) is averaged by the charge and discharge current recorded at 0 V (vs Hg/HgO).

**Fe-incorporation test of Ni/LIG.** This test was done on Ni/LIG. The catalyst (on glassy carbon electrode) was cycled from 1.21 to 1.53 V (vs RHE) in 1 M KOH with slow magnetic stirring (60 rpm). The Fe-containing electrolyte was prepared by adding 100 \( \mu \)L of 1 M FeCl\(_3\) into 100 mL 1 M KOH and then the suspension was stirred for 6 h. The excess Fe precipitated, ensuring soluble Fe\(^{3+}\) saturated the 1 M KOH solution. For the Fe-incorporation test, the electrode was cycled in 1 M KOH for 20 cycles prior to further cycling in the Fe-containing electrolyte.
Calculation of the turnover frequency (TOF). The turnover frequency represents the number of catalytic cycles occurring at the active center per unit time and is generally calculated as: TOF (s$^{-1}$) = (number of oxygen turnover)/(number of active sites) = ($j/4F$)/$n$, where $j$ is the current density at a specific overpotential (e.g. 300 mV) and $n$ is the number of active sites calculated based on the ICP-OES result. The number of oxygen turnover is calculated with Equation 4.3:

\[ (j \text{ mA cm}^{-2})(\frac{1 \text{ C}}{1000 \text{ mA}})(\frac{1 \text{ mol e}^{-}}{96485 \text{ C}})(\frac{1 \text{ mol O}_2}{4 \text{ mol e}^{-}}) \times N_A \]

Equation 4.3. TOF calculation of the NiFe/LIG catalysts.

4.2.2. Result and Discussion

The in situ synthesis of NiFe/LIG catalysts were done by a laser assisted method as shown in Figure 4.1. Briefly, the LIG was patterned on a piece of PI sheet followed by UV-ozone treatment to increase the hydrophilicity. Then the precursor solution containing Ni$^{2+}$ and Fe$^{3+}$ was dropped onto the LIG. Due to the increased hydrophilicity and porosity of LIG, the solution was uniformly adsorbed by the carbon structure. After drying, we lased the PI sheet again atop the original LIG. The extremely high local temperature (>2500 °C) generated while the underlying PI film was being graphitized facilitates the nucleation process of the metal ions, leading to a metal oxide/graphene composite structure. The NiFe/LIG catalysts were prepared based on 3 different Ni:Fe molar ratios of the precursor solutions,$^{174}$ 2:1 for NiFe/LIG-
1, 1:1 for NiFe/LIG-2 and 1:2 for NiFe/LIG-3, along with Ni/LIG (1:0) and Fe/LIG (0:1) for comparison. Unlike the previously reported method, the current method does not require the solubility/compatibility of metal precursors in poly(amic acid) solutions, nor the utilization of chemical vapor deposition system (CVD). All of the procedures can be directly done on the PI sheet in the ambient environment and water solvent.

Figure 4.1. Preparation of the NiFe/LIG catalysts and the SEM images. (b) NiFe/LIG-1, (c) NiFe/LIG-2 and (d) NiFe/LIG-3. The scale bar represents 10 µm.

Figure 4.2. SEM images of NiFe/LIG-1.
The scanning electron microscopy (SEM) images shown in Figure 4.1, Figure 4.2, Figure 4.3 and Figure 4.4 illustrate the morphology of the catalysts. Regardless of the different Ni:Fe ratio, the catalysts show a highly porous structure with no nanoparticle aggregates. The catalysts are powders for which the sheet conductivity could not be measured, but prior work shows the porous LIG graphitic structure maximizes the exposure of the surface active sites and contributes to a good electric conductivity for electrochemical reactions.
Figure 4.5. TEM images and Raman spectra of the NiFe/LIG catalysts. (a) NiFe/LIG-1, (b) NiFe/LIG-2 and (c) NiFe/LIG-3. The scale bar represents 10 nm.

The transmission electron microscopy (TEM) image shown in Figure 4.5 revealed the nanoparticle/graphene hybrid structure. The nanoparticles are well embedded in the graphene structure and surrounded by a few layers of graphene. For NiFe/LIG-1 and NiFe/LIG-3, the size of the nanoparticles is ~10-15 nm. NiFe/LIG-2 has a smaller nanoparticle size of ~5-12 nm, indicating a higher surface area compared to NiFe/LIG-1 and NiFe/LIG-3. The NiO phase planar spacing of the (211)
plane (0.21 nm) was clearly observed from the high-resolution images. Figure 4.5d demonstrates the graphene structure in the catalysts (see also Figure 4.6). The clearly identified D, G and 2D peaks suggest the existence of defected or bent multilayer graphene as the characteristic sign of LIG, which is consistent with the TEM observations. The results confirmed that the nanoparticles and LIG were formed during the laser scribing.

Figure 4.6. Powder XRD diffraction pattern of the catalysts and supplementary Raman spectra and TEM images. Solid rhombus (◆) represents the pattern from NiO, open rhombus (◇) represents the pattern from Ni0, and solid roundness (●) represents the pattern from Fe₂O₃. (b) Raman spectra of Ni/LIG and Fe/LIG. And the TEM images of (c) Ni/LIG and (d) Fe/LIG.
Figure 4.7. XPS analysis of the NiFe/LIG catalysts. The high-resolution spectra in (a) Ni 2p, (b) Fe 2p, (c) C 1s and (d) O 1s regions (The satellite peak is abbreviated as sat.).

X-ray photoelectron spectroscopy (XPS) measurements were performed to analyze the elemental composition and chemical valence states of the catalysts. The results are summarized in Figure 4.7. The Ni 2p$_{3/2}$ region of the NiFe/LIG catalysts shows two main peaks at ~852.8 and ~855.8 eV that can be attributed to the Ni$^0$ and Ni$^{2+}$ with the split spin-orbit components at ~870.1 and 873.1 eV, respectively.\textsuperscript{187} The Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ peaks locates at 710.8 and 729.3 eV alone with the satellite peaks, which are the characteristic binding energies of Fe$^{3+}$.\textsuperscript{188} These features indicate the existence of small amount of elemental Ni in the catalysts that might be caused by the reduction at high temperature induced by the laser. However, the Ni$^0$ would be oxidized to Ni$^{2+}$ and further to Ni$^{3+}$ under anodic conditions prior to the OER potentials.\textsuperscript{173}
The C 1s spectra show a characteristic peak of LIG at 284.5 eV, corresponding to the sp$^2$ carbon from graphene. The O 1s spectra has two distinct peaks: the peak at ~532 eV originates from the oxygen-containing moieties such as C-O and C=O from LIG; and the peak at ~530 eV corresponds to the metal oxides. In addition to the XPS measurement, the ratios of Ni:Fe are determined by the inductively coupled plasma optical emission spectrometry (ICP-OES). The molar ratios of Ni:Fe are 61:39, 46:54 and 33:67 for NiFe/LIG-1, NiFe/LIG-2 and NiFe/LIG-3, respectively.

Although the signal to noise ratio of the XRD patterns in Figure 4.6 is low, we can still find the characteristic peaks that help to understand the bulk composition of the catalysts. The broad peak at ~26° corresponds to the (002) planes of multilayer graphene (LIG). Fe/LIG shows a broad (311) peak at ~35°, however, this peak becomes very weak and nearly indistinguishable from the noise in the NiFe/LIG catalysts. This result shows that most of the Fe species are not in the form of monometallic oxide (Fe$_2$O$_3$). Ni/LIG shows characteristic peaks from both Ni0 ((110) peak at ~39° and (111) peak at ~44°) and NiO ((111) at ~37° and (200) at 43°), both approximately the same height. This is consistent with the XPS result (Figure 4.7) and TEM images (Figure 4.6). Comparison of the Ni$^0$ peak in the Ni/LIG catalyst to the same position in the NiFe/LIG catalysts shows a reduction in size in the NiFe/LIG catalyst, especially when compared to the NiO peak from the NiFe/LIG catalysts. Figure 4.6b shows the Raman spectra of the Fe/LIG and Ni/LIG catalysts for comparison to the Raman spectra for the NiFe/LIG catalysts in Figure 4.5. The clearly
identified D, G and 2D peaks suggest the characteristic multi-layer graphene structure of LIG which is consistent with the TEM images.

Figure 4.8. TEM elemental mapping of the catalysts.

The elemental maps of Ni and Fe (Figure 4.8) show that the distribution of Fe species overlaps well with that of the Ni, suggesting that the nanoparticles consist of both Ni and Fe. The XRD result (Figure 4.6a) indicates that there are few separate phases of Fe in the NiFe/LIG catalysts, in contrast to those found in the Fe/LIG (Fe$_2$O$_3$). Also, the high resolution TEM images of the NiFe/LIG catalysts indicate little Fe$_2$O$_3$, but the characteristic lattice plane spacing of NiO was observed. By combining the
results from high resolution TEM, XRD and elemental mapping, we conclude that the Fe species are mainly doped in the NiO nanoparticles.

Figure 4.9. OER performance characterized in 1 M KOH. (a) LSV curves recorded at 2 mV s⁻¹. (b) Tafel plots calculated from the LSV curves. (c) Comparison of the Tafel slopes and $\eta_{10}$ of the catalysts with IrO₂ nanoparticles$^{81}$ (◇) and 3D Ir$^{189}$ (☆). (d) Stability test, potential profile of the catalysts for bulk OER at 10 mA cm$^{-2}$.

The OER activity of the NiFe/LIG catalysts along with Ni/LIG and Fe/LIG was assessed in 1 M KOH using a 3-electrode configuration. Figure 4.9a shows the linear sweep voltammetry (LSV) curves recorded at 2 mV s⁻¹. The NiFe/LIG catalysts
exhibited much higher activities than either Ni/LIG or Fe/LIG. The OER onset potentials of the NiFe/LIG catalysts are \( \sim 210 \text{ mV} \) despite overlapping with the Ni oxidation peak.\(^{190}\) In contrast, the onset potentials of Ni/LIG and Fe/LIG are much higher at 250 and 290 mV, respectively. The current density \( (j) \) of NiFe/LIG-2 reached 10 mA cm\(^{-2}\) at a remarkably low overpotential \( (\eta_{10}) \) of 240 mV. The \( \eta_{10} \) of NiFe/LIG-1 and NiFe/LIG-3 are 266 and 279 mV, respectively. Conversely, the \( \eta_{10} \) of Ni/LIG is very high at 380 mV and that of Fe/LIG is even higher at 395 mV. The NiFe/LIG-1 and NiFe/LIG-2 rose to \( j \) of 100 mA cm\(^{-2}\) at very low overpotentials of 324 and 309 mV (Figure 4.10), indicating the intrinsic high activity of the catalysts. Figure 4.11 shows the galvanostatic OER performance of NiFe/LIG-2. The catalyst exhibited excellent stability at \( j \) ranging from 10 to 100 mA cm\(^{-2}\). It should be noted that a slight variation of the potential during the bulk OER is reasonable due to the formation and desorption of bubbles on the electrode surface. The reaction kinetics was characterized by the Tafel plots shown in Figure 4.9b.\(^{154}\) The binary metal oxide based catalysts have shown significantly improved OER kinetics over the monometallic oxides. The NiFe/LIG-2 has an impressively low Tafel slope of 32.8 mV dec\(^{-1}\), followed by 33.4 mV dec\(^{-1}\) for NiFe/LIG-1 and 36.6 mV dec\(^{-1}\) for NiFe/LIG-3.

Figure 4.9c provides a straightforward comparison of the catalysts with the benchmarking Ir-based catalysts in terms of \( \eta_{10} \) and Tafel slope. The NiFe/LIG catalysts demonstrated much higher activity than the IrO\(_2\) nanoparticles.\(^{81}\) The NiFe/LIG-2 even have a comparable performance to that of the 3D Ir catalyst.\(^{189}\) A detailed comparison of NiFe/LIG catalysts with state-of-the-art Ni-Fe OER catalysts is
summarized in Table 4.1, where the NiFe/LIG catalysts stand out for their superior OER activity in addition to the simple and feasible preparation method. In addition to for the high OER activity, the NiFe/LIG catalysts showed excellent durability throughout the test (Figure 4.9d). After 15000 s of bulk OER at 10 mA cm\(^{-2}\), the \(\eta_{10}\) slightly increased by 11, 12 and 34 mV for NiFe/LIG-1, NiFe/LIG-2 and NiFe/LIG-3, respectively.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Preparation method(^a)</th>
<th>Tafel Slope (mV dec(^{-1}))</th>
<th>(\eta_{10}) mA cm(^{-2}) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe/LIG-1</td>
<td>LIG</td>
<td>33.4</td>
<td>266</td>
</tr>
<tr>
<td>NiFe/LIG-2</td>
<td>LIG</td>
<td>32.8</td>
<td>240</td>
</tr>
<tr>
<td>NiFe/LIG-3</td>
<td>LIG</td>
<td>36.6</td>
<td>279</td>
</tr>
<tr>
<td>NiFe LDH(^{182})</td>
<td>PLAL</td>
<td>47.6</td>
<td>280</td>
</tr>
<tr>
<td>Ni-Fe/3D-ErGO(^{191})</td>
<td>ED</td>
<td>33</td>
<td>259</td>
</tr>
<tr>
<td>Ni-Fe(^{191})</td>
<td>ED</td>
<td>58</td>
<td>331</td>
</tr>
<tr>
<td>NiFe LDH(^{81})</td>
<td>PC</td>
<td>67</td>
<td>347</td>
</tr>
<tr>
<td>NiFe LDH/CNT hybrid(^{93})</td>
<td>PC</td>
<td>31</td>
<td>247</td>
</tr>
<tr>
<td>FeNi LDH(^{180})</td>
<td>PC</td>
<td>48</td>
<td>232</td>
</tr>
</tbody>
</table>

\(^a\)
Table 4.1. Comparison of the NiFe/LIG catalysts with recently reported OER catalysts.

*Abbreviations for the methods: LIG, this work; PLAL, pulsed laser ablation in liquid; ED, electrodeposition; PC, precipitation; IA, iron incorporation by aging; EX, exfoliation.

| NiFe LDH exfoliated | EX from PC | 40 | 302 |

![Figure 4.10. LSV curves of the catalysts at high potential.](image)

![Figure 4.10. LSV curves of the catalysts at high potential.](image)
Figure 4.11. Galvanostatic OER performance of NiFe/LIG-2 ramping from 10 to 20, 40, 60, 80 and 100 mA cm$^{-2}$ in 1 M KOH.

Figure 4.12. Electrochemical analysis of the catalysts. (a) CV curves recorded in 1 M KOH at 2 mV s$^{-1}$. (b) Geometric current density ($j_{GSA}$) at 0 V (vs Hg/HgO) plotted against the scan rate for the determination of $C_{dl}$. (c) EIS of the catalysts. Inset shows the equivalent circuit to simulate the $R_S$ and $R_{CT}$. (d) TOF and mass activity of the catalysts at 300 mV overpotential.

The results above have shown that the NiFe/LIG catalysts have much lower thermodynamic and kinetic barriers than either Ni/LIG or Fe/LIG. In order to further
understand the high activity of the catalysts, we performed cyclic voltammetry measurements (CV) as depicted in Figure 4.12a. The data were collected at a low scan rate (2 mV s\(^{-1}\)) to ensure a quasi-equilibrium measurement. There is no feature associated with the change in the oxidation state of Fe as suggested by previous reports.\(^{174}\) On the contrary, a pair of anodic and cathodic waves was observed in the Ni-containing catalysts, which was attributed to the redox of Ni\(^{2+}\) to higher oxidation states (Ni\(^{3+}\) and Ni\(^{4+}\)).\(^{194}\) The redox waves shifted anodically and decreased gradually as the Fe content increased. For NiFe/LIG-2 and NiFe/LIG-3 (where the Fe content is 54\% and 67\%, respectively), the anodic wave started to overlap with the OER current. It is evident that the presence of Fe suppressed the oxidation of Ni\(^{2+}\) to higher oxidation states, however, the underlying mechanism is still under debate.\(^{194}\) Several hypotheses have been proposed, for example, the decreased affinity to oxygen of the Ni surface\(^{195}\) and the destabilization of Ni\(^{3+}\) species in presence of Fe\(^{3+}\).\(^{196}\) Additionally, it was also revealed that the effective conductivity of the catalysts was sensitive to the Fe content, which might also contribute to the redox behavior of the NiFe-based catalyst.\(^{194}\)

Our results are in accord with the NiFe catalysts synthesized by solution-based methods where the maximum performance is achieved with Fe content of ~15-50\% while further increasing Fe content would decrease the activity.\(^{77}\) In light of recent studies regarding the crucial effect of Fe on the local activity of Ni(OH)\(_2\)/NiOOH,\(^{197}\) we carried out a Fe-incorporation test of Ni/LIG (see below Figure 4.13). In the electrolyte without intentionally added Fe\(^{3+}\), the Ni/LIG showed nearly no increase in
the OER activity (300 mV overpotential) after 300 CV cycles. On the contrary, an immediate increase in the OER activity was observed when the electrode was moved into the Fe-containing electrolyte, suggesting a rapid Fe incorporation.\textsuperscript{197} We also noticed that the change in the OER activity upon gradual Fe incorporation was not directly related to the shifts of the peak position of Ni\textsuperscript{2+}/Ni\textsuperscript{3+} redox. Our findings coincide with the mechanism proposed by Boettcher et al.,\textsuperscript{197} indicating that the OER activity depends more on the Fe incorporated at the edges/surface defects of Ni(OH)\textsubscript{2}/NiOOH than on the Fe inside the bulk nanoparticles. And it might be the case that the rapid laser heating would lead to more surface defects of the nanoparticles as compared with other solution based methods.\textsuperscript{65} It is likely that the Fe sites incorporated at the surface of γ-NiOOH account for the highest activity for their lowest overpotential proposed by theoretical calculations.\textsuperscript{195} On the other hand, the measured redox curve of Ni\textsuperscript{2+}/Ni\textsuperscript{3+} (Figure 4.12a) represents a cumulative result over the bulk nanoparticles and so that the electrochemical behavior of the active sites might be averaged in the CV measurements.
Figure 4.13. Fe-incorporation test of Ni/LIG.
(a) CV curves of Ni/LIG in 1 M KOH without intentionally added Fe. (b) The CV curves of 1st, 25th and 300th cycle from (a). (c) CV curves of Ni/LOH in Fe-containing electrolyte. The initial 20 cycles were recorded in 1 M KOH without intentionally added Fe. (d) The CV curves of 75th and 200th cycle from (c), and that of NiFe/LIG-2. (e) and (f) show the current density at 300 mV overpotential ($j_{\eta300}$) and anodic Ni$^{2+}$/Ni$^{3+}$ peak position ($E_{anodic}$) as a function of the cycle number adapted from (a) and (c), respectively.
Recent studies have shown that Fe impurities would readily incorporate into Ni(OH)$_2$/NiOOH during electrochemical measurements.\textsuperscript{85} Figure 4.13a and b show the CV curves of Ni/LIG in 1 M KOH with the current density at 300 mV overpotential ($j_{\eta300}$) and anodic Ni$^{2+}$/Ni$^{3+}$ peak position ($E_{\text{anodic}}$) plotted against the cycles in Figure 4.13e. In initial cycles (1~25), the $E_{\text{anodic}}$ shifted to low potential and as peak slightly narrowed and increased. The shift of $E_{\text{anodic}}$ should be due to the formation of more ordered Ni(OH)$_2$/NiOOH. After the 25$^{th}$ cycle, the $E_{\text{anodic}}$ shifted anodically and the peak decreased gradually. At 300$^{th}$ cycle, the $E_{\text{anodic}}$ was 29 mV higher than that of 25$^{th}$ cycle. However, the $j_{\eta300}$ did not show much change during the entire cycling. The mere change in $E_{\text{anodic}}$ could be explained by the presence of trace amount of Fe in the electrolyte and the results are in consistent with a recent study by Boettcher \textit{et al.}\textsuperscript{194} Nevertheless, it should be noted that, the trace Fe impurities has little effect on the OER performance of our catalysts since the $j_{\eta300}$ is far lower than those of the NiFe/LIG catalysts.

The Fe-incorporation test of Ni/LIG was done in the electrolyte with intentionally add Fe$^{3+}$ as shown in Figure 4.13c. The initial 20 cycles were recorded in 1 M KOH and the subsequent cycles were done in the Fe-containing electrolyte. When the electrode was moved into the Fe-containing electrolyte at 21$^{th}$ cycle, immediate increases in both $E_{\text{anodic}}$ (by 8 mV) and $j_{\eta300}$ (by 1.5 mA cm$^{-2}$) were observed. Further cycling resulted in the gradual increase of $j_{\eta300}$ till its maximum value of 12.8 mA cm$^{-2}$ at $\sim$75$^{th}$ cycle, where the $E_{\text{anodic}}$ was 22 mV anodically shifted than that of
21th cycle. After ~75th cycle, the \( E_{\text{anodic}} \) kept increasing while the \( j_{\eta300} \) decreased. At 200th cycle, the \( E_{\text{anodic}} \) and \( j_{\eta300} \) were 1.404 V (vs RHE) and 7.1 mA cm\(^{-2} \), respectively.

In our measurement, the gradually shifted \( E_{\text{anodic}} \) with decreased intensity agreed well with the long-held opinion that Fe suppressed the oxidation of Ni\(^{2+} \) to higher valence state (+3 and +4).\(^{174} \) However, the results also revealed that \( j_{\eta300} \) is not directly related with \( E_{\text{anodic}} \). As shown in Figure 4.13d, the OER activity of 200th cycle was inferior to that of 75th cycle, despite the more suppressed Ni\(^{2+}/Ni^{3+} \) redox. In consideration of our catalysts which are nanoparticles with diameter of ~10-20 nm embedded in graphene, it is reasonable to assume that the Fe would firstly incorporate at the edges/surface defects, and further move inside of the bulk nanoparticle. On the other hand, the effective conductivity of NiOOH remains high through the potential window and it is not decreased by the Fe incorporation.\(^{194} \) Therefore, the measured Ni\(^{2+}/Ni^{3+} \) redox would be a cumulative result of the whole nanoparticle. Since the OER activity is more dependent on the surface structure of the heterogeneous catalyst, the immediate change at 21th cycle should be induced by the instant Fe incorporation at the edges/surface defects of Ni(OH)\(_2\)/NiOOH. Since the edges/surface defects are gradually incorporated as the cycling continued, the rate of current increase reduced and the \( j_{\eta300} \) reached the maximum value at~75th cycle (Figure 4.13f). The decrease of \( j_{\eta300} \) upon further cycling were caused by several reasons, such as the formation of FeOOH phase on the surface of NiOOH and the distorted bulk structure after Fe incorporation. Whereas, since the measured \( E_{\text{anodic}} \) is related to the bulk nanoparticle, it kept increasing as Fe was incorporated.
Our results coincide with the recent study on Ni(OH)$_2$ thin film$^{197}$ suggesting the effects of Fe on the local structure. The active species based on our catalyst is likely to be the NiOOH with Fe incorporated at the edges/surface defects. And the enhanced activity was attributed to the partial charge transfer between Ni and Fe.$^{194}$ It’s worth noting that although the efficient catalyst could be prepared by Fe incorporation, our LIG method provides a more convenient and scalable way to produce catalyst with better performance (Figure 4.13d).

In addition to the inherent activity of the active sites, the electrochemically active surface area (EASA) is also important to the overall catalytic performance since it determines the total active sites exposed to the electrolyte.$^{79}$ Figure 4.12b illustrates the double-layer capacitance ($C_{dl}$) calculated from the CV curves (Figure 4.14). Benefiting from the porosity and conductivity of LIG, the catalysts have reasonably high $C_{dl}$ of 1.76, 3.06 and 1.20 mF cm$^{-2}$ for NiFe/LIG-1, NiFe/LIG-2 and NiFe/LIG-3, respectively. And the corresponding EASA are about 44, 76 and 30 cm$^2$ per cm$^2$ of the geometric surface area (GSA), respectively. The electrochemical impedance spectrum (EIS) was used to study the reaction kinetics under OER conditions (Figure 4.15).$^{193}$ As shown in Figure 4.12c, NiFe/LIG-2 has a remarkably low charge transfer resistance ($R_{CT}$) of 15 Ω under 280 mV overpotential, and the $R_{CT}$ further decreased to 8 Ω under 300 mV overpotential (Figure 4.15d). The $R_{CT}$ of NiFe/LIG-1 and NiFe/LIG-3 are slightly higher as 22 and 66 Ω, respectively, in concert with their lower activities than that of NiFe/LIG-2. The large EASA is beneficial for the intimate contact of the catalysts with the electrolyte, along with the exposure of active
sites to ensure an efficient charge transfer between the electrode and the electrolyte that contributes to the excellent OER activity.

Figure 4.14. Determination of the $C_{dl}$.
CV curves recorded at 10, 20, 40, 60, 80 and 100 mV s$^{-1}$ of the catalysts.
Figure 4.15. EIS of the catalysts at different overpotentials and the $R_{CT}$. 
In order to provide an indication of the activity of a specific site, we calculated the turnover frequency (TOF) by averaging over the total moles of metal ions (Ni and Fe) based on the $j$ at 300 mV overpotential.\(^{174}\) Table 4.2 summarizes data from the NiFe/LIG catalysts and compares it to recently published results. The NiFe/LIG catalysts have comparatively high TOF with a high mass loading of $\sim 0.265$ mg cm\(^{-2}\). The highest TOF of 0.42 s\(^{-1}\) is achieved on NiFe/LIG-2 with a $j$ of 85.70 mA cm\(^{-2}\) at 1.53 V. The $j$ is also of much importance since it demonstrates the specific mass activity of the catalyst, although a higher TOF is usually calculated from low mass loading. Another notable phenomenon is that the carbon-composited catalysts generally have much higher activities than the unsupported ones, and this includes the exfoliated LDHs that have a high surface-volume ratio.\(^{190}\) As summarized in Table 4.3, the catalysts have high current density (86 mA cm\(^{-2}\)), high TOF (0.42 s\(^{-1}\)) along with high mass activity (323 mA mg\(^{-1}\)). The NiFe/LIG catalysts have shown comparable performance to the ones prepared by more elaborate solution-based processes.
<table>
<thead>
<tr>
<th>Catalysts</th>
<th>$j$ (mA cm$^{-2}$)</th>
<th>TOF (s$^{-1}$)</th>
<th>Mass loading (mg cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/LIG</td>
<td>0.95</td>
<td>$2.0 \times 10^{-3}$</td>
<td>$\sim 0.265$</td>
</tr>
<tr>
<td>NiFe/LIG-1</td>
<td>51.99</td>
<td>$2.6 \times 10^{-1}$</td>
<td>$\sim 0.265$</td>
</tr>
<tr>
<td>NiFe/LIG-2</td>
<td>85.70</td>
<td>$4.2 \times 10^{-1}$</td>
<td>$\sim 0.265$</td>
</tr>
<tr>
<td>NiFe/LIG-3</td>
<td>28.15</td>
<td>$1.1 \times 10^{-1}$</td>
<td>$\sim 0.265$</td>
</tr>
<tr>
<td>Fe/LIG</td>
<td>0.20</td>
<td>$6.2 \times 10^{-4}$</td>
<td>$\sim 0.265$</td>
</tr>
<tr>
<td>NiFe LDH$^{81}$</td>
<td>5.5</td>
<td>$1.0 \times 10^{-2}$</td>
<td>0.07</td>
</tr>
<tr>
<td>NiFe LDH exfoliated$^{81}$</td>
<td>9.35</td>
<td>$5.0 \times 10^{-2}$</td>
<td>0.07</td>
</tr>
<tr>
<td>NiFeO$_x$ film$^{85}$</td>
<td>1.24</td>
<td>$2.1 \times 10^{-1}$</td>
<td>0.0012</td>
</tr>
<tr>
<td>Fe:Ni(OH)$_2$ film$^{192}$</td>
<td>25-28</td>
<td>1.5</td>
<td>30 nm of active layer</td>
</tr>
<tr>
<td>FeNi LDH$^{180}$</td>
<td>Not reported</td>
<td>$2.8 \times 10^{-2}$</td>
<td>0.25</td>
</tr>
<tr>
<td>FeNi-rGO LDH hybrid$^{180}$</td>
<td>Not reported</td>
<td>$9.9 \times 10^{-1}$</td>
<td>0.25</td>
</tr>
<tr>
<td>NiFe LDH/CNT hybrid</td>
<td>Not reported</td>
<td>$5.6 \times 10^{-1}$</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Table 4.2. Comparison of catalyst activity with recent published works (1.53 V vs RHE).
Table 4.3. TOF and mass activity of the catalysts at 250 and 300 mV overpotentials.

The OER performance could be further improved by loading the catalysts on a porous substrate, such as the Ni foam. Benefiting from the high surface area and high conductivity of Ni foam, the NiFe/LIG-2@NF showed a remarkably high $j$ of 400 mA cm$^{-2}$ at a very low overpotential of 354 mV as shown in Figure 4.16a.
Figure 4.16. OER performance of the catalyst loaded on Ni foam and carbon fiber paper. (a) LSV curve of the NiFe/LIG-2 loaded on Ni foam (~0.5 mg cm$^{-2}$). (b) The OER performance of NiFe/CFP in 1 M KOH. Inset shows the corresponding Tafel plots.

In addition to the LIG/PI substrate, our method also worked on other compatible substrates. The CO$_2$ laser is widely used for the manufacturing of carbon fiber based materials due to the significant thermal input from the incident laser beam. Therefore, the thermal effect could be utilized to prompt the nucleation of metal oxides. Following a procedure similar to that for NiFe/LIG, we prepared the free-standing NiFe/CFP electrodes, where the catalyst was formed in situ on the CFP through the laser scribing process. Figure 4.16b illustrates the excellent OER performance of NiFe/CFP, the onset potential ~1.45 V and $j$ reaching 100 mA cm$^{-2}$ at 285 mV overpotential with a Tafel slope of 89 mV dec$^{-1}$. These results not only provide a feasible method for the preparation of self-supported catalytic electrodes, but also demonstrate the wide breadth of the LIG method for the synthesis of various catalysts.
4.2.3. Conclusion

In summary, we developed a straightforward and feasible method for the \textit{in situ} synthesis of highly efficient OER catalysts through the LIG. By loading the metal precursor on LIG followed by laser scribing, the strategy afforded NiFe/LIG catalysts \textit{via} a solid phase transition process that did not require CVD or cumbersome solution-based reactions. The catalysts show remarkably high OER activity and excellent stability in alkaline electrolyte. The onset potential is ~210 mV and the lowest Tafel slope is 32.8 mV dec$^{-1}$. Furthermore, our method works well on the CFP substrate so as to provide a convenient way for the preparation of a free-standing catalytic electrode. More importantly, the method we presented is potentially available for the facile synthesis of a variety of catalysts in addition to the NiFe-based OER catalysts. Our findings may lead to further improvements on the design and scalable production of efficient catalysts that works for other electrochemical reactions.

4.3. Experimental Contributions

\textbf{Jibo Zhang} designed part of the experiments, prepared the samples, and conducted part of the characterizations including Raman, XPS, electrochemical measurements and etc. \textbf{Muqing Ren} designed part of the experiments and conducted part of the characterizations including SEM, TEM, XRD and ICP-OES. \textbf{Yilun Li} helped in SEM and TEM.
Laser-Induced Graphene with Bifunctional Catalysts for Metal-Oxygen Batteries

This chapter was entirely copied from reference.¹⁹⁹

5.1. Introduction

The rapid economic development and increasing consumption of carbon fuels have spawned high CO₂ emissions.²⁰⁰,²⁰¹ This increase, coupled with the awareness of climate change, has prompted the development of carbon neutral and renewable energy. Recently, rechargeable metal-O₂ batteries have garnered increasing attention as efficient energy-storage systems due to their considerably high theoretical energy densities.¹⁰⁵,²⁰²-²⁰⁴ In contrast to conventional batteries, metal-O₂ batteries feature an open cell structure so that the cathode material, O₂, can be obtained from the ambient atmosphere.²⁰⁵,²⁰⁶
Metal-O\textsubscript{2} batteries exhibit high energy densities. For example, Li metal possesses a high theoretical specific energy (\textasciitilde3600 Wh kg\textsuperscript{-1}), with a high cell voltage (nominally 2.96 V) in a Li-O\textsubscript{2} battery.\textsuperscript{207, 208} Similarly, the Zn-O\textsubscript{2} system stands out for its high specific energy density (\textasciitilde1080 Wh kg\textsuperscript{-1}) and volumetric energy density (\textasciitilde6100 Wh L\textsuperscript{-1}) in aqueous electrolytes.\textsuperscript{208, 209} However, the overall reactions of oxygen at the cathode in the rechargeable metal-O\textsubscript{2} batteries, known as the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), are often hindered by sluggish kinetics that lead to a decrease in both energy and power densities of the batteries.\textsuperscript{210, 211} Therefore, the development of efficient bifunctional electrocatalysts for both ORR and OER is of great importance to enhance the performance of metal-O\textsubscript{2} batteries.

Generally, the noble metal-based materials, such as Pt,\textsuperscript{212, 213} Pd,\textsuperscript{214, 215} Ir\textsuperscript{216} and Ru,\textsuperscript{217} are highly efficient for electrocatalysis in metal-O\textsubscript{2} batteries, but practical applications are severely limited by their high cost and scarcity. Considerable efforts have also been devoted to the development of noble metal-free bifunctional electrocatalysts, such as the nitrogen-doped graphene and carbon nanotubes,\textsuperscript{119, 218} first-row transition metal oxides,\textsuperscript{219} perovskite oxides,\textsuperscript{220} and graphene composites\textsuperscript{221, 222} catalysts.

The synthesis of the catalysts generally consists of two major approaches: wet chemistry methods such as hydro-/solvothermal reactions, and thermal annealing/pyrolysis processes. Recently, our group developed a facile method to produce porous graphene by direct laser writing on a polyimide (PI) sheet to produce
laser-induced graphene (LIG). LIG has high porosity, good electrical conductivity and chemical stability, all of which are conducive to the development of porous materials for efficient cathode catalysts. Based on this technique, we further develop approaches for the in situ formation of metal oxide/LIG composites for either OER or ORR. We present here a straightforward method for the syntheses of highly efficient bifunctional OER/ORR catalysts combining both advantages of the LIG and cobalt oxides. The catalyst is synthesized by one-step laser scribing on the precursor-loaded LIG/PI sheet that does not require any further liquid phase reactions, post thermal annealing or pyrolysis. The resultant Co₃O₄/LIG shows remarkably high OER/ORR activities, with performances comparable to the noble metal-based catalysts in alkaline electrolyte. Moreover, the Co₃O₄/LIG demonstrates high activity as the cathode material for both aprotic Li-O₂ and aqueous Zn-air batteries. The batteries exhibited low overpotentials in both charge and discharge processes with improved durability. This report regarding LIG-assisted synthesis of bifunctional catalysts in the solid phase might even be beneficial for the synthesis of other transition metal-based catalysts.
5.2. Laser-Induced Graphene with Bifunctional Catalysts for Metal-Oxygen Batteries

5.2.1. Experimental Section

5.2.1.1. Material Synthesis

**Preparation of the catalyst.** All samples were prepared under ambient air following the similar procedures as reported in Chapter 4. Kapton® PI films (McMaster-Carr, Cat. No. 2271K3, thickness: 0.005") were used as received. LIG was generated by a CO₂ laser (10.6 μm, Universal XLS10MWH laser cutter platform) on the PI film in air using 3% of full power and 5% of full speed with an image density of 6. The LIG was patterned on PI as a 2 × 2 cm² structure.

1 M Co(NO₃)₂ solution was prepared with deionized water. The as-prepared LIG (2 × 2 cm²) was treated by the O₂ plasma (Boekel Model 135500) for 1 min to increase the hydrophilicity. 80 μL of the solution were dropped onto the LIG. The soaked LIG (on PI) was dried in air at room temperature overnight and then under vacuum (~120 mm Hg) for 6 h. Then the LIG was lased again atop the previous LIG pattern under the same conditions (3% of full power and 5% of full speed with an image density of 6). Then the powder was scratched off from the PI and collected for further characterization. MnOₓ/LIG was prepared by the same procedures except that the solution was 1 M MnSO₄.
5.2.1.2. Material Characterization

**General characterization.** Scanning electron microscope (SEM) images were obtained by a FEI Quanta 400 high-resolution field emission SEM. Transmission electron microscopy (TEM) images were obtained by a JEOL 2100F field emission gun transmission electron microscope. X-ray photoelectron spectroscopy (XPS) was done by a PHI Quantera SXM scanning X-ray microprobe with a monochromatic 1486.7 eV Al KR X-ray line source, 45° take off angle, and a 200 µm beam size. The XPS spectra were taken from the as-prepared catalysts on PI. Raman spectroscopy was performed at 532 nm laser excitation. ICP-OES was done by a Perkin Elmer Optima 8300 instrument. The material was digested by HNO₃.

**Electrochemical measurements.** Electrochemical measurements were done on a rotating disk electrode (5 mm in diameter, Pine Research Instrumentation). For the preparation of the working electrode, 4 mg of the catalyst and 80 µl of 5 wt% Nafion solution were mixed in 1 mL water/ethanol (4/1, v/v) followed by 2 h bath sonication (Cole Parmer, model 08849-00) to form a homogeneous ink. Then 12 µL of the catalyst ink was dropped onto the glassy carbon electrode and dried under vacuum (~120 mm Hg) at room temperature (the loading is ~0.265 mg cm⁻²). The electrochemical measurements were carried out in a 3-electrode configuration using a CHI 608D electrochemical workstation. A Pt wire and a Hg/HgO electrode (in 1 M KOH) were used as the counter and reference electrodes, respectively. The tests were done in 0.1 M KOH with 95% iR compensation. For the OER test, the scan rate of working electrode was 5 mV s⁻¹ with a rotating speed of 1600 rpm. The number of
electrons transferred \((n)\) during ORR was calculated by the previously discussed Koutecký-Levich (K-L) equation (\textbf{Equation 3.1}) according to the LSV curves with varying rotating speed from 225 to 1600 rpm.

\[
\frac{1}{j} = \frac{1}{j_K} + \frac{1}{j_L} = \frac{1}{j_K} + \frac{1}{B \omega^{1/2}}
\]

\[
B = 0.2nF C_0 D_0^{2/3} \nu^{-1/6}
\]

\textbf{Equation 3.1. Koutecký–Levich equation.}

where \(j\) is the measured current density, and \(j_K\) and \(j_L\) are the kinetic and diffusion-limiting current densities, respectively. \(\omega\) is the rotating speed in rpm, \(F\) is the Faraday constant \((96485 \text{ C mol}^{-1})\), \(C_0\) is the bulk concentration of \(O_2\) \((1.2 \times 10^{-6} \text{ mol cm}^{-3})\), \(D_0\) is the diffusion coefficient of \(O_2\) in 0.1 M KOH \((1.9 \times 10^{-5} \text{ cm}^2 \text{s}^{-1})\), and \(\nu\) is the kinematic viscosity of the electrolyte \((0.01 \text{ cm}^2 \text{s}^{-1})\).

\textbf{Battery test.} The electrochemical performance of \(\text{Co}_3\text{O}_4/LIG\) bifunctional catalysts was tested in lithium-oxygen cells through coin type CR2032 cells. All the cells were assembled in the glove box under argon atmosphere. The CR2032 lithium-oxygen cell includes the lithium foil, Celgard 2500 membrane, 0.5 M lithium bis(trifluoromethanesulfonyl)imide/tetraethylene glycol dimethyl ether (LiTFSI/TEGDME) with 0.05 M LiI and the air cathode electrode. The cathode was prepared by casting slurry which consists 80 wt% catalysts, 10 wt% (Super P, TIMCAL) and 10 wt% polyvinylidene difluoride (PVDF; Alfa Aesar) in \(N\)-methyl-2-pyrrolidone (NMP) on a piece of carbon paper. The galvanostatic discharge/charge
tests were carried out in voltage range of 2.0 to 4.3 V (vs Li/Li⁺). Pure O₂ flow was maintained during the test. The Co₃O₄/LIG cathode for rechargeable Zn-air battery was tested on a home-made device. The electrolyte is 6 M KOH with 0.2 M Zn(OAc)₂. The cathode material was loaded on a carbon fiber paper (~1 mg cm⁻²), and a Zn plate was used as the anode. Pure O₂ flow was maintained during the test.

5.2.2. Result and Discussion

The Co₃O₄/LIG catalyst was prepared by a recently developed LIG-assisted method in the solid phase. As shown in Figure 5.1a, LIG was formed on a PI sheet followed by O₂ plasma treatment to enhance the hydrophilicity of the LIG. Then the precursor aqueous solution, 1 M Co(NO₃)₂, was added to the LIG pattern. The porous LIG with enhanced wettability uniformly adsorbed the solution and therefore the metal salts were well-distributed in the LIG after the drying process. Subsequently, a second laser scribing was carried out atop the treated LIG. The nucleation of Co²⁺ was triggered by the extremely high local temperature when the laser hit the LIG and resulted in the formation of the Co₃O₄/LIG catalyst. In the previously reported synthesis of CoOₓ/LIG, the metal precursor was dissolved in the poly(amic acid), the PI precursor, and a pressurized thermal cycle of 250-300 °C was needed followed by a thermal annealing process at 750 ° C. The present method is not limited to the poly(amic acid) solubility of the metal precursor and it can all be done on the commercial PI film. Also, the resultant Co₃O₄/LIG is directly used as the cathode catalysts for metal-O₂ batteries without any post treatment.
Figure 5.1. Synthesis and characterization of Co$_3$O$_4$/LIG. (a) Preparation of the Co$_3$O$_4$/LIG catalyst. (b) SEM and (c) TEM images of the Co$_3$O$_4$/LIG. The inset HRTEM image shows the lattice planes of Co$_3$O$_4$ nanocrystals.

Figure 5.1b and Figure 5.2 shows the scanning electron microscopy (SEM) images of the Co$_3$O$_4$/LIG at different magnifications. The Co$_3$O$_4$/LIG exhibits a highly porous surface morphology with much graphenic structure opening to the surface, which would contribute to a large active surface area$^{28,161}$ to enable facile mass transport with the electrolyte during the electrochemical reactions. No large particles or aggregates were observed in the SEM images, suggesting a homogeneous distribution of the metal oxide particles in the LIG. The transmission electron microscopy (TEM) images shown in Figure 5.1c illustrate that the nanoparticles are
embedded in the graphene with sizes of 5 to 10 nm. The nanocrystals in Co$_3$O$_4$/LIG display clear lattice fringes in the high-resolution TEM images. The Co$_3$O$_4$ crystal phase planar spacing of the (220), (311) and (111) planes are 0.286, 0.242 and 0.480 nm, respectively. The multilayer graphene structure is also evidenced by the characteristic interplanar spacing of 0.34 nm as shown in Figure 5.3.

![Figure 5.2. SEM images of the Co$_3$O$_4$/LIG at different magnifications.](image-url)
Figure 5.3. TEM images of the Co$_3$O$_4$/LIG.

The structure of Co$_3$O$_4$/LIG was further studied by Raman spectroscopy and X-ray diffraction (XRD). As shown in Figure 5.4a, the peaks at $\sim$1585 and 2700 cm$^{-1}$ of the Raman spectrum correspond to the G and 2D peaks of graphene, respectively. The D band at 1342 cm$^{-1}$ is characteristic of bent graphene layers and defects.$^{226}$ The $I_G/I_{2D}$ ratio is $\sim$2.5, indicating the presence of a multilayer graphenic structure, which is consistent with the observation from the TEM images. The region circled by the dashed line in Figure 5.4a displays the Raman features of Co$_3$O$_4$ as illustrated in Figure 5.4b. Two characteristic peaks at $\sim$470 and 671 cm$^{-1}$ can be assigned to the $E_g$ and $A_{1g}$ modes of Co$_3$O$_4$.\textsuperscript{227} The XRD spectra of Co$_3$O$_4$/LIG further confirmed the
graphenic structure of LIG by a typical (002) peak of graphene at $\sim 26^\circ$ ($d_{002} = 0.34$ nm). The (111), (311), (222) and (422) peaks from crystalline $\text{Co}_3\text{O}_4$ were also observed.\textsuperscript{227}

The amount of Co in the $\text{Co}_3\text{O}_4$/LIG was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). The Co content is $\sim 4.2$ wt%. The chemical composition of the $\text{Co}_3\text{O}_4$/LIG was studied by X-ray photoelectron spectroscopy (XPS). The Co 2$p^{3/2}$ core level region consists of two main peaks at 780 and 782 eV, which indicate the presence of both +2 and +3 oxidation states of Co.\textsuperscript{228} The C 1$s$ spectrum, with a predominant peak centered at 284.5 eV, reveals the graphitic carbon in the catalyst. The O 1$s$ spectrum further shows the C-O and C=O moieties on the LIG.\textsuperscript{122}
Figure 5.4. Characterization of the Co$_3$O$_4$/LIG.
(a-b) Raman spectra of the catalyst, the dashed line indicates the Raman fingerprints of Co$_3$O$_4$. The Raman active modes are $F_{2g}$ (191 cm$^{-1}$, 511 cm$^{-1}$ and 610 cm$^{-1}$), $E_g$ (472 cm$^{-1}$), and $A_{1g}$ (678 cm$^{-1}$). (c) Powder XRD pattern of the Co$_3$O$_4$/LIG. High-resolution XPS spectrum in (d) Co 2p and (e) C 1s and O 1s regions.
Figure 5.5. Electrochemical characterization of the Co$_3$O$_4$/LIG. (a) CV curves of Co$_3$O$_4$/LIG and pristine LIG in O$_2$-saturated 0.1 M KOH at 1600 rpm. (b) OER polarization curves of Co$_3$O$_4$/LIG and pristine LIG at 1600 rpm; the inset shows the corresponding Tafel slope. (c) CV curves of Co$_3$O$_4$/LIG in Ar- and O$_2$-saturated 0.1 M KOH at a scan rate of 20 mV s$^{-1}$. (d) LSV curves for ORR at different rotating speeds in O$_2$-saturated 0.1 M KOH.

The electrocatalytic activity of Co$_3$O$_4$/LIG was characterized using a rotating disk electrode in 0.1 M KOH electrolyte. The cyclic voltammetry (CV) curves in Figure 5.5a show the complete electrocatalytic reactions (ORR and OER) of Co$_3$O$_4$/LIG and pristine LIG at 1600 rpm in O$_2$-saturated electrolyte. The Co$_3$O$_4$/LIG exhibited significantly enhanced current density compared LIG in both OER and ORR despite
the low content of the Co species. A pair of redox peaks was observed for Co\textsubscript{3}O\textsubscript{4}/LIG at \( \sim 1.1 \) V (vs RHE), which are attributed to the faradic reaction for Co-O/Co-OOH\textsuperscript{229}. The OER kinetics were further investigated by linear swept voltammetry (LSV) as shown in **Figure 5.5b**. The Co\textsubscript{3}O\textsubscript{4}/LIG exhibited an onset potential of \( \sim 1.49 \) V, beyond which the current density increased rapidly with a low Tafel slope of 40 mV dec\textsuperscript{1}. The current density reached 10 mA cm\textsuperscript{-2} at 340 mV overpotential. The electrochemical impedance spectra (**Figure 5.6**) also revealed the low charge transfer resistance of 25 \( \Omega \) at 350 mV overpotential. Conversely, pristine LIG suffered from sluggish kinetics with a Tafel slope as high as 135 mV dec\textsuperscript{1}. While the catalyst system here is clearly very easy to prepare in a solvent-free manner, the OER performance of Co\textsubscript{3}O\textsubscript{4}/LIG is comparable or even better than the other Co-based OER catalysts that have been reported as summarized in **Table 5.1**.

![EIS of Co\textsubscript{3}O\textsubscript{4}/LIG at different OER overpotentials in 0.1 M KOH.](image)

**Figure 5.6.** EIS of Co\textsubscript{3}O\textsubscript{4}/LIG at different OER overpotentials in 0.1 M KOH.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Preparation method</th>
<th>Onset $E$ (V)</th>
<th>$\eta_{10}$ (mV)</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Co}_3\text{O}_4$/LIG</td>
<td>LIG</td>
<td>1.49</td>
<td>340</td>
<td>40</td>
</tr>
<tr>
<td>$\text{Co}_3\text{O}_4$/MCNT$^{230}$</td>
<td>Hydrothermal</td>
<td>1.51</td>
<td>390</td>
<td>65</td>
</tr>
<tr>
<td>$\text{Co}_3\text{O}_4$/C nanowires$^{231}$</td>
<td>Hydrothermal and thermal annealing</td>
<td>1.47</td>
<td>290</td>
<td>70</td>
</tr>
<tr>
<td>Au-meso-$\text{Co}_3\text{O}_4$$^{232}$</td>
<td>Nanocasting method</td>
<td>1.53</td>
<td>440</td>
<td>46</td>
</tr>
<tr>
<td>meso-$\text{Co}_3\text{O}_4$$^{233}$</td>
<td>Template method</td>
<td>-</td>
<td>411</td>
<td>80</td>
</tr>
<tr>
<td>Hollow Ni-Co oxide$^{234}$</td>
<td>NaBH$_4$ reduction</td>
<td>1.501</td>
<td>362</td>
<td>61.4</td>
</tr>
<tr>
<td>$\text{Mn}<em>x\text{Co}</em>{3-x}\text{O}_4-\delta$$^{235}$</td>
<td>Self-templating</td>
<td>1.52</td>
<td>350</td>
<td>85</td>
</tr>
<tr>
<td>NiCo LDH nanosheets$^{236}$</td>
<td>Solvothermal</td>
<td>1.52</td>
<td>420</td>
<td>113</td>
</tr>
<tr>
<td>ZnCo LDH/graphene$^{237}$</td>
<td>Co-precipitation</td>
<td>1.56</td>
<td>430</td>
<td>73</td>
</tr>
</tbody>
</table>

**Table 5.1. Comparison of the $\text{Co}_3\text{O}_4$/LIG catalysts with Co-based OER catalysts (in 0.1 M KOH).**

**Figure 5.5c** displays the CV curves of $\text{Co}_3\text{O}_4$/LIG for ORR in Ar- and O$_2$-saturated electrolyte. Despite any disturbances caused by O$_2$ bubbling as seen by the small-peak riddled, the current density sharply increased with an $E_{1/2}$ redox peaks of
O$_2$/OH$^-$ at 0.72 V, suggesting an efficient reduction of O$_2$ to OH$^-$. The Co$_3$O$_4$/LIG showed an improved activity compared to LIG (Figure 5.7), and the low ORR Tafel slope of 70 mV dec$^{-1}$ (Figure 5.8) is comparable to those of graphene-based composites such as Fe-N-rGO (~110 mV dec$^{-1}$)$^{238}$ and Co$_3$O$_4$/N-rmGO (~42 mV dec$^{-1}$)$^{223}$ The ORR kinetics was further assessed by LSV at different rotating speeds. Linear fitting of the K-L plots reveals an electron-transfer number ($n$) of ~3.5 at the selected potentials (Figure 5.8b), demonstrating that the ORR by Co$_3$O$_4$/LIG is dominated by a four-electron transfer pathway (O$_2$ to OH$^-$). The slight deviation of $n$ from 4 might be caused by the carbon surfaces as observed for conductive carbon supported catalysts.$^{159}$

Figure 5.7. LSV curves of Co$_3$O$_4$/LIG and LIG in O$_2$-saturated 0.1 M KOH at 1600 rpm.
Figure 5.8. Supplementary ORR data for Co₃O₄/LIG. (a) LSV curves of Co₃O₄/LIG for ORR, inset shows the Tafel slope. (b) K-L plots of Co₃O₄/LIG.

The bifunctional catalytic activity of Co₃O₄/LIG was characterized by the difference in potential between the selected OER current density (10 mA cm⁻²) and ORR current density (-3 mA cm⁻²). The values are summarized in Table 5.2. The $E_{\text{OER}} - E_{\text{ORR}}$ of Co₃O₄/LIG is 0.98 V, which is slightly higher than that of Ir/C (0.92 V), but still remarkably lower than that of Pt/C (1.16 V) and Ru/C (1.01 V). In addition, the Co₃O₄/LIG shows higher bifunctional activity than the Co- and Mn-based catalysts prepared by hydrothermal reaction or electrodeposition (Table 5.2). The smaller the value is, the lower the overpotential that is required to reach a specific current for either OER or ORR, which is essential to lower the overpotential for charge and discharge process in metal-O₂ batteries.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Preparation method&lt;sup&gt;a&lt;/sup&gt;</th>
<th>( E_{\text{ORR}} ) (V) at -3 mA cm(^{-2})</th>
<th>( E_{\text{OER}} ) (V) at 10 mA cm(^{-2})</th>
<th>( E_{\text{OER}}-E_{\text{ORR}} ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Co}_3\text{O}_4/\text{LIG} )</td>
<td>LIG</td>
<td>0.59</td>
<td>1.57</td>
<td>0.98</td>
</tr>
<tr>
<td>20 wt% Ir/C&lt;sup&gt;239&lt;/sup&gt;</td>
<td>-</td>
<td>0.69</td>
<td>1.61</td>
<td>0.92</td>
</tr>
<tr>
<td>20 wt% Pt/C&lt;sup&gt;239&lt;/sup&gt;</td>
<td>-</td>
<td>0.86</td>
<td>2.02</td>
<td>1.16</td>
</tr>
<tr>
<td>20 wt% Ru/C&lt;sup&gt;239&lt;/sup&gt;</td>
<td>-</td>
<td>0.61</td>
<td>1.62</td>
<td>1.01</td>
</tr>
<tr>
<td>( \text{Co}_3\text{O}_4 )&lt;sup&gt;240&lt;/sup&gt;</td>
<td>HT</td>
<td>0.61</td>
<td>1.74</td>
<td>1.13</td>
</tr>
<tr>
<td>( \text{Co(OH)}_2 )&lt;sup&gt;240&lt;/sup&gt;</td>
<td>HT</td>
<td>0.66</td>
<td>1.68</td>
<td>1.02</td>
</tr>
<tr>
<td>( \text{NiCo}_2\text{O}_4/\text{G} )&lt;sup&gt;241&lt;/sup&gt;</td>
<td>HT</td>
<td>0.54</td>
<td>1.67</td>
<td>1.13</td>
</tr>
<tr>
<td>Mn oxide&lt;sup&gt;239&lt;/sup&gt;</td>
<td>ED</td>
<td>0.73</td>
<td>1.77</td>
<td>1.04</td>
</tr>
</tbody>
</table>

Table 5.2. Comparison of the \( \text{Co}_3\text{O}_4/\text{LIG} \) catalysts with recently reported OER/ORR bifunctional catalysts.

<sup>a</sup>Abbreviation: HT: hydrothermal reaction; ED: electrodeposition.
Figure 5.9. Zn-air battery with Co$_3$O$_4$/LIG as the cathode catalyst.
(a) Open-circuit voltage and (b) the power density and charge/discharge polarization plots. The galvanostatic discharge and charge cycling curves of the rechargeable battery at (c) 2 mA cm$^{-2}$ and (d) 10 mA cm$^{-2}$. (e) Long-term cycling performance of the battery at 2 mA cm$^{-2}$ (360 s per cycle).
In consideration of the excellent bifunctionality of Co$_3$O$_4$/LIG, we fabricated a homemade Zn-air battery using the gas diffusion layer (carbon fiber paper, CFP) loaded with catalysts (1 mg cm$^{-2}$) for the cathode, with a Zn plate as the anode and 0.2 M Zn(OAc)$_2$ in 6 M KOH as the electrolyte. The battery exhibited a high open-circuit voltage of 1.46 V (Figure 5.9). Figure 5.9b displays the charge and discharge polarization curves with the corresponding power density. The power density reached 47.6 mW cm$^{-2}$ at 50 mA cm$^{-2}$, and further reached 84.2 mW cm$^{-2}$ at 100 mA cm$^{-2}$ (Figure 5.10). An ideal bifunctional catalyst should possess high discharge voltage, low charge voltage and reversibility. Figure 5.9c and Figure 5.9d show the galvanostatic charge/discharge profile at 2 and 10 mA cm$^{-2}$, respectively. The battery showed a remarkably stable charging voltage of 2.01 V and a discharge voltage of 1.24 V at 2 mA cm$^{-2}$. The voltage gap between charge and discharge increased to 0.96 V at
10 mA cm\(^2\). The Zn-air battery also exhibited very good cycling stability as shown in Figure 5.9e. The voltage gap slightly increased from 0.86 V to 1.01 V after 190 cycles. Therefore, the Co\(_3\)O\(_4\)/LIG has shown promising applicability as the cathode for Zn-air batteries with a high round-trip efficiency and notable stability.

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**Figure 5.11.** Characterization of the Co\(_3\)O\(_4\)/LIG cathode in Li-O\(_2\) battery. (a) Galvanostatic cycling performance of the Co\(_3\)O\(_4\)/LIG electrode at a current density of 0.08 mA cm\(^2\) with limited capacity of 430 mAh g\(^{-1}\); (b) first discharge and charge profile of the cyclic performance; (c) discharge capacity and terminal voltage versus cycle number; (d) charge capacity and terminal voltage versus cycle number.
The electrocatalytic activity of Co$_3$O$_4$/LIG was further examined in Li-O$_2$ batteries using a coin cell architecture with 0.5 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and in 0.05 M LiI in tetraethylene glycol dimethyl ether (TEGDME) as the electrolyte. Figure 5.11a shows the galvanostatic charge/discharge profile of the cell in the first 100 cycles with a cut-off capacity of 430 mAh g$^{-1}$. The voltage gap of the charge/discharge process at the 1$^{st}$ cycle was as low as 0.42 V (Figure 5.11b). The discharge voltage of Co$_3$O$_4$/LIG cell was ~2.73 V (vs Li$^+$/Li) in the 1$^{st}$ cycle and slightly decreased to ~2.67 V in the 100$^{th}$ cycle; both were close to the theoretical discharge voltage (2.96 V), suggesting a stable energy output of the cell.$^{242}$

The Li-O$_2$ battery exhibited outstanding cycle stability as shown in Figure 5.11c and Figure 5.11d. The charge/discharge terminal voltage and capacity (within 2.0 to 4.3 V) were plotted against the cycle number. The discharge capacity reached 430 mAh g$^{-1}$ for 242 cycles with a slightly decreased discharge terminal voltage from 2.73 V to 2.40 V of the 242$^{nd}$ cycle. Similarly, the charge terminal voltage increased to 3.73 V at 100$^{th}$ cycle and further to 4.3V at 242$^{nd}$ cycle. The rapid decrease of capacity starting at the ~245$^{st}$ cycle together with the significant increase of the overpotentials might be caused by several factors, such as the electrolyte drying out and/or the cathode becoming covered by insulating byproducts. In comparison, the pristine CFP current collector showed poor cyclability of up to 20 cycles in the same voltage window (Figure 5.12). The charge/discharge terminal voltage increased/decreased rapidly within the first few cycles. Therefore, the capacity from the current collector
was negligible since the Co₃O₄/LIG possessed much higher activity. It is worth noting that the Co₃O₄/LIG also showed remarkable stability in air. Figure 5.13 illustrates the cycle stability of the battery working in purified air (CO₂ and moisture removed by filtration) for up to 98 cycles. Because of the low overpotential of the Co₃O₄/LIG electrode, the decomposition of the electrolyte and oxidation of carbon support was minimized, resulting in a long battery cycle life.²⁴³

Figure 5.12. Galvanostatic cycling performance of an CFP electrode at a current density of 0.08 mA cm⁻².
The electrochemical reaction of O₂ in the cell was investigated by CV in Ar and O₂ atmosphere. Figure 5.14a displays the data recorded between 2.0 and 4.5 V with a scan rate of 0.5 mV s\(^{-1}\) obtained after 1\(^{st}\) cycle. In Ar, the current density was very low and did not show any significant peak. Both the cathodic and anodic currents increased in O₂ atmosphere, indicating the ORR of O₂ and the OER of the Li₂O₂, respectively. The ORR onset is ~2.77 V, very close to 2.96 V, suggesting the high inherent oxygen reduction activity of Co₃O₄/LIG. The OER onset potential is ~3.15 V, but the overpotentials for both ORR and OER slightly increase as the cell cycles due to the formation of byproducts and incomplete decomposition of discharge products.\(^{160}\) The electrochemical impedance spectra (EIS) were also measured to study the intrinsic behavior of the Li-O₂ battery during cycling. Figure 5.14b shows...
the EIS recorded at the initial stage and the end of first discharge/charge process under open circuit voltage. The equivalent serial resistance remained nearly the same, however, the charge transfer resistance increased from \( \sim 200 \, \Omega \) to \( \sim 450 \, \Omega \). This increase in the interfacial resistance might be caused by the poor electrically conductive products at the electrode/electrolyte interface, which remains a typical hurdle for current Li-O\(_2\) batteries\(^{160}\). The LIG-assisted method also works well for the preparation of bifunctional catalysts based on other transition metals in addition to Co, for example, Mn. Figure 5.15 shows the XPS and cycling performance for MnO\(_x\)/LIG in a Li-O\(_2\) battery. Although the performance was not as high as in the Co\(_3\)O\(_4\)/LIG, the MnO\(_x\)/LIG cathode showed considerable stability for \( \sim 100 \) cycles.

Figure 5.14. Electrochemical analysis of the Li-O\(_2\) battery.
(a) CV curves of the battery in Ar and O\(_2\) atmosphere. (b) EIS of the battery.
Figure 5.15. MnO\textsubscript{x}/LIG cathode for Li-O\textsubscript{2} battery.
(a) XPS spectrum of MnO\textsubscript{x}/LIG and the cycling performance of MnO\textsubscript{x}/LIG as the cathode for Li-O\textsubscript{2} battery in (b) O\textsubscript{2} and (c) purified air.

5.2.3. Conclusion

In this study, we demonstrated the solid phase synthesis of an OER/ORR bifunctional catalyst, Co\textsubscript{3}O\textsubscript{4}/LIG, through a facile LIG-based process. Benefiting from the high porosity and conductivity of LIG with the intrinsic high activity of Co\textsubscript{3}O\textsubscript{4}, the Co\textsubscript{3}O\textsubscript{4}/LIG exhibited high activity for OER and ORR in alkaline media. These favorable properties further led to the enhancement performance of Co\textsubscript{3}O\textsubscript{4}/LIG as a cathode
material for metal-air batteries. The $\text{Co}_3\text{O}_4$/LIG worked well as an efficient cathode material for the aqueous Zn-air battery as well as the aprotic Li-O$_2$ battery. The batteries showed low overpotentials in both charge and discharge processes combined with excellent cycling durability. In addition to the notable catalytic performance of $\text{Co}_3\text{O}_4$/LIG, the facile synthetic method brings about a new way for the design and synthesis of bifunctional and multifunctional catalysts. This contribution is expected to encourage further development in the carbon-metal oxide composited cathodes for metal-air batteries using the LIG approach.

5.3. Experimental Contributions

Jibo Zhang designed the experiments, prepared the samples, and conducted part of the characterizations including Raman, XPS, ICP-OES, electrochemical measurements etc. Muqing Ren designed part of the experiments and conducted part of the characterizations including SEM, TEM, XRD and battery test.
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