Effect of Vinylethylene Carbonate and Fluoroethylene Carbonate Electrolyte Additives on the Performance of Lithia-Based Cathodes

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ABSTRACT: Nanolithia-based materials are promising lithium-ion battery cathodes owing to their high capacity, low over-potential, and stable cyclic performance. Their properties are highly dependent on the structure and composition of the catalysts, which play a role in activating the lithia to participate in the electrochemical redox reaction. However, the use of electrolyte additives can be an efficient approach to improve properties of the lithia-based cathodes. In this work, vinylethylene carbonate (VEC) and fluoroethylene carbonate (FEC) were introduced as electrolyte additives in cells containing lithia-based cathode (lithia/(Ir, Li2IrO3) nanocomposite). The use of additives enhanced the electrochemical performance of the lithia-based cathodes, including the rate capability and cyclic performance. Especially, their available capacity increased without modifying the cathodes. Results of X-ray photoelectron spectroscopy (XPS) analysis confirmed that the additives form interface layers at the cathode surface, which contain Li2CO3, more carbon reactants, and more LiF than the interface layer formed with the pristine electrolyte. The Li2CO3 and carbon reactants may improve rate capability by facilitating Li+ transport, and LiF may stabilize the Li2O2 (and/or LiO2) produced by the oxygen redox reaction with lithia. Therefore, the additive-enhanced electrochemical performance of the cell is attributed to the effects of the interface layer derived from additive decomposition during cycling.

INTRODUCTION

In recent years, lithium-ion batteries (LIBs) have been used in various devices, including smartphones, laptop computers, and electric vehicles. As the applications of LIBs increase, the demand for advanced LIBs with high energy densities increases as well. Developing high-capacity cathodes is indispensable for realizing advanced LIBs with high energy densities. Since the commercialization of LIBs with LiCoO2 as the cathode material, many transition-metal oxides, such as Li(Ni, Co, Mn)O2 (NCM)1−3 and Li(Ni, Co, Al)O2 (NCA),4−7 have been suggested as advanced cathode materials with higher capacities. The capacity of these transition-metal oxides is fundamentally based on the cationic redox reaction of the transition-metal ions in the oxides. These cathode materials have also been successfully commercialized owing to their considerable capacities and stable electrochemical performances. However, because the discharge capacity of these oxides is determined by the amount of transition metal present, the weight of the transition metals has prevented higher capacity results.

Recently, new cathode materials based on anionic redox reactions have attracted much attention. They are expected to deliver a higher capacity than that of commercial cathodes because the anionic redox reaction is attributed to the oxidation and reduction of oxygen, which has a lighter weight than transition metals. In practice, several cathode materials, such as Li−Nb−Mn−O, Li−Mn−O, and Li−Ru−M−O (M = Sn, Nb), have yielded capacities that exceed 300 mAh·g−1.8−15 Although their capacity is based on both the cationic redox reaction associated with transition metals and the anionic (oxygen) redox reaction, the latter is more influential. However, these materials have exhibited sluggish kinetics and rapid capacity fading during cycling.

Lithia (Li2O)-based materials are also promising cathode materials based on the anionic redox reaction.16−21 In contrast to that of commonly used cathode materials, the capacity of lithia-based cathodes is attributed primarily to the oxygen (anionic) redox reaction between O2− (Li2O) and O− (0.5 ≤ x < 2). They also have superior cyclic characteristics compared to those of Li−M−O (M = Nb, Mn, Ru, Sn, etc.) cathodes.16−18 However, the electrochemically inactive lithia (Li2O) must be combined with catalysts (sometimes called...
dopants) to activate the anionic redox reaction. The catalysts also stabilize vulnerable reaction products, such as Li$_2$O$_2$ and/or LiO$_2$. Therefore, selecting both a suitable catalyst and the specific lithia/catalyst combination has been a focus of research on lithia-based cathodes.

As a new approach, the introduction of an electrolyte additive has recently been suggested as a method of enhancing the electrochemical performance of lithia-based cathodes without changing the type of catalyst or the structure of the lithia-catalyst nanocomposites. However, little research has been conducted on these additives thus far, and the cause of the additive effect is not yet known. In this study, the effect of electrolyte additives on the electrochemical properties of a lithia-based cathode was characterized in detail. Specifically, we attempted to clarify the cause of the additive effect by analyzing the interface layer derived from the additives. A lithia/(Ir, Li$_2$IrO$_3$) nanocomposite was used as a lithia-based cathode owing to its high capacity and stable cyclic performance. Vinylenethylene carbonate (VEC) and fluoroethylene carbonate (FEC) were used as electrolyte additives because they are generally applied to enhance the electrochemical performance of the Li-ion cells. Including additives was expected to increase the available capacity of the lithia/(Ir, Li$_2$IrO$_3$) nanocomposite due to the formation of an interface layer during cycling. The interface layer formed on the nanocomposite was analyzed using X-ray photoelectron spectroscopy (XPS) to elucidate the effect of the additives.

**RESULTS AND DISCUSSION**

Figure 1 shows the voltage curve of the lithia/(Ir, Li$_2$IrO$_3$) nanocomposite for three cycles measured at a current density of 10 mA·g$^{-1}$. Three types of electrolytes, pristine (ethylene carbonate/dimethyl carbonate, EC/DMC = 1:1), FEC-added, and VEC-added electrolytes, were used, and the capacity was limited to 600 and 700 mAh·g$^{-1}$ to determine the limit of available capacity of the samples. Lithia-based cathodes generate oxygen gas when they are overcharged beyond the capacity limit at which oxygen maintains the condensed phase, a result of which it is necessary to determine the available capacity that can be stably used with sufficient cyclic performance. The capacity was calculated based on the lithia weight in the electrode. As shown in Figure 1a, when the capacity was limited to 600 mAh·g$^{-1}$ and the pristine electrolyte was used, the voltage curves retained their capacity for three cycles. However, the overpotential observed in the voltage curve gradually increased during cycling. When the
limited capacity was increased to 700 mAh·g⁻¹ (Figure 1b), the discharge capacity was not maintained and began to decrease in the third cycle. This indicates that 700 mAh·g⁻¹ exceeded the available capacity of the lithia/(Ir, Li₂IrO₃) nanocomposite in these conditions.

Notably, the shape of the voltage curves of the lithia/(Ir, Li₂IrO₃) nanocomposite was changed significantly by the additives. When the FEC-added electrolyte was used, the voltage curve of the nanocomposite at a limited capacity of 600 mAh·g⁻¹, measured in (a) pristine electrolyte, (b) FEC-added electrolyte, and (c) VEC-added electrolyte.

Figure 2. Voltage profiles of lithia/(Ir, Li₂IrO₃) nanocomposites at current densities of 10, 50, 100, and 200 mA·g⁻¹ with a limited capacity of 600 mAh·g⁻¹, obtained using (a) pristine electrolyte, (b) FEC-added electrolyte, and (c) VEC-added electrolyte.

Figure 3. Cyclic performance of lithia/(Ir, Li₂IrO₃) nanocomposites at a current density of 100 mA·g⁻¹ with a limited capacity of 600 mAh·g⁻¹, measured in (a) pristine electrolyte, (b) FEC-added electrolyte, and (c) VEC-added electrolyte.
increased to 700 mAh g\(^{-1}\), the voltage profile was somewhat changed during the three cycles and the overpotential increased compared to that measured with a limited capacity of 600 mAh g\(^{-1}\) (Figure 1d).

As shown in Figure 1e,f, the voltage curve of the nanocomposite measured using the VEC-added electrolyte also showed a lower overpotential than that measured using the pristine electrolyte. In particular, when the capacity was limited to 700 mAh g\(^{-1}\), the VEC-added electrolyte considerably reduced the overpotential of the cell compared to the over-potentials measured using the FEC-added and the pristine electrolytes. These results indicate that the use of additives successfully increased the available capacity of the lithia/(Ir, Li\(_2\)IrO\(_3\)) nanocomposite and reduced the overpotential of the cells. Furthermore, VEC seems to be more efficient in obtaining these effects than FEC.

Figure 2 compares the initial voltage profiles of the lithia/(Ir, Li\(_2\)IrO\(_3\)) nanocomposite measured at current densities of 10, 50, 100, and 200 mA g\(^{-1}\) using each of the three electrolytes at a limited capacity of 600 mAh g\(^{-1}\). When the pristine electrolyte was used, the cells showed rapid capacity reduction as the current density increased (Figure 2a). In contrast, the cells maintained their capacity (600 mAh g\(^{-1}\)), even at high current densities (100 and 200 mA g\(^{-1}\)), when the FEC- and VEC-added electrolytes were used, as shown in Figure 2b,c. Moreover, the increase in overpotential at high current densities (100 and 200 mA g\(^{-1}\)) was reduced by the use of additives. These results demonstrate that including FEC and VEC additives in the electrolyte is an effective method for enhancing the rate capability of the lithia/(Ir, Li\(_2\)IrO\(_3\)) nanocomposite as well as increasing the capacity of the cell.

Adding VEC to the electrolyte seems to be more efficient than adding FEC in reducing the overpotential and improving the rate capability of the lithia/(Ir, Li\(_2\)IrO\(_3\)) nanocomposite.

The cyclic performance of the lithia/(Ir, Li\(_2\)IrO\(_3\)) nanocomposite was measured using each of the three electrolytes, with a current density of 100 mA g\(^{-1}\) and a limited capacity of 600 mAh g\(^{-1}\). As shown in Figure 3a, the capacity of the cell was reduced after a few cycles with a limited capacity of 600 mAh g\(^{-1}\) when using the pristine electrolyte. This indicates that the cell was overcharged beyond the available capacity of the lithia/(Ir, Li\(_2\)IrO\(_3\)) nanocomposite in these conditions. In general, it is assumed that the lithia (Li\(_2\)O, O\(^{2-}\)) can be oxidized to peroxide (Li\(_2\)O\(_2\), O\(^{1-}\)) during charging while retaining the condensed oxygen phase. Moreover, it has also been suggested that the oxygen in the lithia could be oxidized to LiO\(_2\) (O\(^{0.5-}\)) during charging without oxygen evolution, which would lead to an increase in the theoretical capacity of lithia from 897 to 1341 mAh g\(^{-1}\). Considering this, the limited capacity of 600 mAh g\(^{-1}\) adopted in this work is lower than the theoretical capacity of the lithia. However, the electrochemical activation of lithia is difficult and a suitable catalyst is required to activate the oxygen redox reaction in the lithia. In this study, the Li\(_2\)IrO\(_3\) and Ir (generated from the decomposition of Li\(_2\)IrO\(_3\)) acted as catalysts. Because the milling process used during the preparation of the cathode material results in imperfect contact between the lithia and the catalysts, some portions of lithia may not be electrochemically activated, which results in the capacity being lower than the theoretical capacity. Therefore, the limited capacity of 600 mAh g\(^{-1}\) can be inferred to be beyond the achievable capacity while maintaining the condensed phase.

Figure 4. Nyquist plots of the lithia/(Ir, Li\(_2\)IrO\(_3\)) nanocomposites obtained using pristine, FEC-added, and VEC-added electrolytes (a) before the electrochemical test, (b) after the first cycle, and (c) after the 100th cycle.
However, the available capacity was increased using FEC and VEC as electrolyte additives without altering the structure or composition of the cathode materials. As shown in Figure 3b, when the FEC was added to the electrolyte, the lithia/(Ir, Li$_2$IrO$_3$) nanocomposite maintained the capacity (600 mAh·g$^{-1}$) during 100 cycles. Although the cell with the VEC-added electrolyte showed slight instability after 83 cycles (Figure 3c), the cyclic performance was clearly improved by the addition of both FEC and VEC to the electrolyte. Considering that the contact between lithia and catalysts in the cathode materials is not modified due to the effect of electrolyte additives, the increase in capacity achieved using electrolyte additives cannot be easily explained by changes in the cathodes themselves.

The reaction products of the oxygen redox reaction in lithia-based cathodes, such as Li$_2$O$_2$ and/or LiO$_2$, are difficult to retain within the structure of the condensed phase because they are unstable and highly reactive. The stabilization of these reaction products in the lithia-based cathode is one of the purposes of using catalysts; however, the unstable reaction products may be able to react with other materials, such as the electrolyte, despite the inclusion of catalysts in the cathode material. In particular, Li$_2$O$_2$ and LiO$_2$ are expected to be able to easy release electrons into the electrolyte and release gaseous oxygen in the fully charged state. Therefore, the ability to suppress these undesirable Li$_2$O$_2$ and LiO$_2$ reactions is one of the major factors in determining the available capacity of the lithia-based cathodes. The authors believe that the electrolyte additives may assist in the stabilization of the oxygen redox reaction products during cycling. In previous studies, FEC and VEC have been applied to the formation of a solid–electrolyte interphase (SEI) layer in the cell to protect the electrode from the electrolyte and they have been used to form a protective film on the anode surface. However, FEC and VEC can also form an interface layer on the cathode surface, which may help to protect Li$_2$O$_2$ and LiO$_2$ from undesirable reactions with the electrolyte, resulting in an increase in the capacity of lithia-based cathodes.

Figure 4 shows the Nyquist plots of the cells containing the lithia/(Ir, Li$_2$IrO$_3$) nanocomposite, measured before the electrochemical test, after the first cycle, and after the 100th cycle (with a limited capacity of 600 mAh·g$^{-1}$) using each of the three electrolytes. The semicircle in the Nyquist plots indicates the impedance value of the cells, which is related to the charge-transfer resistance and the SEI layer. The size of the semicircle in the Nyquist plots obtained before the electrochemical test was reduced by including the FEC and VEC electrolyte additives, which indicates that the additives effectively reduced the impedance value of the cell (Figure 4a). The addition of VEC showed this effect more clearly than the addition of FEC. The semicircle size measured using the pristine electrolyte did not change distinctly after the first cycle; however, the size of the semicircles decreased slightly after the first cycle when the electrolyte additives were used. The relatively low impedance of the cells with electrolyte additives can explain the superior rate capability and low overpotential observed in Figures 1 and 2. This also shows that the use of FEC and VEC facilitates the charge transfer and decreases the resistance related to the SEI layer. Furthermore, VEC is more effective than FEC in reducing the impedance of the cells. As shown in Figure 4c, the impedance of all cells was...
increased after the 100th cycle. Particularly, the cell using the pristine electrolyte showed a significantly increased impedance value, while the cells using electrolyte additives showed relatively less increased impedance value.

To elucidate the effect of the FEC and VEC electrolyte additives on the electrochemical performance of the lithium-based cathodes, the surface layer of the cathode was analyzed using scanning electron microscopy (SEM) and XPS. Figure 5 shows the SEM images of the electrode surfaces before and after 100 cycles using each of the three electrolytes and a limited capacity of 600 mAh·g⁻¹. The surface of the electrodes is composed of a cathode (lithia/(Ir, Li₂IrO₃) nanocomposite), conductive carbon, and a binder (poly(vinylidene difluoride), PVDF). In the SEM image of the cathode obtained before the electrochemical test, protruding powder particles are clearly observed (Figure 5a), although it is difficult to distinguish individual components clearly. However, after cycling, the powder particles appear to be covered with a film layer (Figure 5b−d), which may be formed during cycling.

For a more detailed analysis, the surface of the electrodes was analyzed by XPS after 100 cycles using each of the three electrolytes and a limited capacity of 600 mAh·g⁻¹. Figure 6a shows the C 1s spectrum of the cathode after 100 cycles using the pristine electrolyte. The peak at approximately 284.6 eV was assigned to the C−C bond and related to the conductive carbon in the electrode. The peaks observed at approximately 291.0 and 285.4 eV are attributed to the CF₂ and C−H environments of the binder (PVDF), respectively. The peaks at about 286.5 and 287.6 eV correspond to C−O−C and CO₂ due to carbon reactants present on the surface, respectively, which may be derived from the decomposition of the carbonate electrolyte during cycling. In the F 1s spectrum (Figure 6b), the peak observed at approximately 688.1 eV was attributed to C−F₂ in the PVDF binder in the electrode. The other peaks at approximately 685.5 and 687 eV arise from LiF and Li_xPO_yF_z, respectively, which are generated from the decomposition of the LiPF₆ salt-containing electrolyte during cycling. In the F 1s spectrum (Figure 6b), the peak observed at approximately 291.0 and 285.4 eV are attributed to the CF₂ and C−H environments of the binder (PVDF), respectively. The peaks at about 286.5 and 287.6 eV correspond to C−O−C and CO₂ due to carbon reactants present on the surface, respectively, which may be derived from the decomposition of the carbonate electrolyte during cycling. In the F 1s spectrum (Figure 6b), the peak observed at approximately 688.1 eV was attributed to C−F₂ in the PVDF binder in the electrode. The other peaks at approximately 685.5 and 687 eV arise from LiF and Li_xPO_yF_z, respectively, which are generated from the decomposition of the LiPF₆ salt-containing electrolyte during cycling. In the F 1s spectrum (Figure 6b), the peak observed at approximately 688.1 eV was attributed to C−F₂ in the PVDF binder in the electrode. The other peaks at approximately 685.5 and 687 eV arise from LiF and Li_xPO_yF_z, respectively, which are generated from the decomposition of the LiPF₆ salt-containing electrolyte during cycling.
288.2 eV were attributed to Li$_2$CO$_3$ and the polar carbonate \((R\text{-CO}_2)\), respectively, which were newly generated, and the intensity of the peak corresponding to C–O=C (286.5 eV) on the surface increased considerably. These species are thought to be derived from the decomposition of the FEC during cycling.\textsuperscript{26} The Li$_2$CO$_3$ and carbon reactants have been reported to facilitate Li\textsuperscript{+} transport, which would enhance the rate capability of the cells using the FEC-added electrolyte,\textsuperscript{26} as shown in Figure 2. In the F 1s spectrum of the electrode cycled in the FEC-added electrolyte (Figure 6d), the peaks were identified as belonging to C–F, LiF, and Li$_2$PO$_4$F, as for the spectrum of the electrode cycled in the pristine electrolyte. However, the relative intensity of the LiF peak increased, while the intensity of the Li$_2$PO$_4$F peak decreased due to the addition of FEC to the electrolyte. The LiF is a stable layer that passivates the electrode surface and suppresses electron leakage from the cathode to the electrolyte.\textsuperscript{28} The large proportion of LiF in the interface film layer may play an important role in preventing undesirable reactions between the electrolyte and reactive Li$_2$O$_2$ (and/or LiO$_2$) species formed by the oxygen redox reaction in the lithia-based cathode.

In the C 1s spectrum of the electrode cycled in the VEC-added electrolyte (Figure 6e), the intensity of the peaks related to Li$_2$CO$_3$ and carbon reactants (C–O=C, C–H) was significantly larger compared to that of other C 1s spectra (Figure 6a,c). This suggests that using VEC as the electrolyte additive results in the formation of a higher quantity of the carbon species (including Li$_2$CO$_3$) during cycling compared with that using FEC as the electrolyte additive or using the pristine electrolyte. Considering that Li$_2$CO$_3$ and carbon reactants can enhance the charge transfer of the lithia-based cathode, it is consistent with the fact that the cell using the FEC-added electrolyte showed superior rate capability compared to that of the cells using either the FEC-added electrolyte or the pristine electrolyte. In the F 1s spectrum (Figure 6f), the peak corresponding to LiF is also larger than the peak corresponding to Li$_2$PO$_4$F. The LiF layer can suppress undesirable reactions between the electrolyte and Li$_2$O$_2$ (and/or LiO$_2$). However, the relative intensity of the LiF/Li$_2$PO$_4$F was somewhat lower than that in the spectra of the cells using the FEC-added electrolyte. It is inferred that the LiF layer is formed more easily from the decomposition of FEC than that of VEC because FEC contains fluorine, while VEC does not.

Based on the XPS results, the effect of the electrolyte additives is concluded to arise from the interface layer formed as the additives decompose during cycling. The Li$_2$CO$_3$ and carbon reactants in the interface layer improve the rate capability by facilitating charge transfer. This improvement in the high-rate characteristics of the cell allows more lithia to react with lithium ions and electrons under constant current density conditions and can delay the oxygen evolution caused by local overcharge at the interface. These effects can increase the available capacity of the lithia-based cathode, as shown in Figure 1. The addition of VEC to the electrolyte solution seems to be more effective than the addition of FEC as VEC apparently forms more of these reactants during cycling. The large portion of LiF in the interface layer may stabilize the reactive Li$_2$O$_2$ and LiO$_2$ during cycling, which also helps to increase the available capacity and improve the cyclic performance of the lithia-based cathode. For the formation of the LiF layer, FEC seems to be a more effective electrode additive than VEC, which may explain the fact that the cells using FEC have superior cyclic performance compared to that of the cells using VEC, as shown in Figure 3. The LiF layer can act as an obstacle to the movement of Li ions and electrons during cycling, but in the cycling process, the effect of stabilizing the lithia-based cathode by the formation of a LiF layer will outweigh the drawbacks of the LiF layer because the oxygen reduction reaction products, such as Li$_2$O$_2$ and/or LiO$_2$, are unstable. Figure 7 illustrates the effect of additives in the electrolyte on the lithia-based cathode.

**CONCLUSIONS**

In this study, the effect of FEC and VEC electrolyte additives on the electrochemical performance of a lithia-based cathode (lithia/(Ir, Li$_2$IrO$_3$) nanocomposites) was investigated. Cells using electrolyte additives exhibited increased available capacity, enhanced rate capability, and lower impedance values than those of the cells using the pristine electrolyte. The interface layer, formed due to the decomposition of the electrolyte additives, containing Li$_2$CO$_3$ and carbon reactants on the cathode surface was determined using XPS. The Li$_2$CO$_3$ and carbon reactants facilitate Li\textsuperscript{+} transport, which enhances...
the rate capability and reduces the impedance value of the lithia-based cathodes. The use of VEC as the electrolyte additive was superior in obtaining this effect compared to the use of FEC because VEC generated more Li2CO3 and carbon reactants than FEC. The use of additives also increased the ratio of LiF in the interface layer, which is beneficial to stabilizing the reactive Li2O2 (and/or LiO2) species formed from the oxygen redox reaction in the lithia-based cathodes. Using FEC formed more LiF than that using VEC, which may explain the better cyclic performance of the cells using the FEC-added electrolyte compared to that of the cells using the VEC-added electrolyte. The increased available capacity of the lithia-based cathode achieved by the use of electrolyte additives is attributed to the synergistic effect of stabilizing Li2O2 (and/or LiO2) and improving the rate capability. It is our hope that this work can contribute to the understanding of the effect of electrolyte additives on the performance of the lithia-based cathode.

**METHODS**

To fabricate the Li2IrO3 catalyst, pellets composed of a 1:1.2 (wt %) ratio of IrO2 (Alfa Aesar, 99%) and Li2CO3 (Aldrich, 99.99%) were prepared. The pellets were calcined at 950 °C for 10 h, further heat-treated at 1000 °C for 86 h under an O2 atmosphere, and ground into a powder. The ramping rate was 100 °C h⁻¹ (furnace cooling). The prepared Li2IrO3 powder was used as the catalyst source for the lithia-based nanocomposite. The lithia/(Ir, Li2IrO3) nanocomposite was fabricated by high milling synthesis. The obtained Li2IrO3 powder was dispersed in butanol (Aldrich, anhydrous, 99.8%) with lithia powder (Li2O, Alfa Aesar, 99.5%). The mole ratio of the Li2O (lithia)/Li2IrO3 was 4.5:1. The dried product was mixed using a planetary mono mill (Pulverisette 6, FRITSCH) at 600 rpm for 150 h (resting for 30 min after milling for 1 h). Some Li2IrO3 decomposed to Ir to facilitate the lithia/(Ir, Li2IrO3) nanocomposite formation during the milling process. To prepare the cathode material for use in electrochemical cells, the nanocomposite was mixed with 30 wt % carbon nanotubes and 10 wt % poly(vinylidene fluoride) binder in N-methyl-2-pyrrolidone (NMP), as the solvent, by ball milling for 90 min. Then, the mixture was cast onto aluminum foil and dried under vacuum at 80 °C for 24 h. Coin cells (2032-type) were used for the electrochemical tests with Li metal as the anode and polypropylene as the separator. The electrolyte solution was 1 M LiPF6 dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) of a volume ratio of 1:1. Charge–discharge tests between 1.5 and 4.35 V were performed using an electrochemical workstation (AMETEK, VersaSTAT 3) by applying an AC voltage with an amplitude of 5 mV over a frequency range of 0.1 Hz to 100 kHz. Scanning electron microscopy (SEM, AP tech TECNAI G2 F30 S-Twin) was employed to observe the surface layer of the cathode electrode after cycling. The C 1s and F 1s chemical binding energies of the samples were analyzed by XPS (Thermo Scientific K- α). To prepare the used electrodes for XPS analysis, they were washed several times with DMC and dried under vacuum for 24 h. The obtained spectra were calibrated to the C 1s peak at 284.8 eV.

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**Author Contributions**

Y.J.P. designed the overall research. S.Y.L. conducted the experiments. S.Y.L. and Y.J.P. wrote the manuscript.

**Notes**

The authors declare no competing financial interest.

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