Carbon-free Polymer Air Electrode based on Highly Conductive PEDOT Micro-Particles for Li-O₂ Batteries

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ABSTRACT

This study introduced a carbon-free electrode for Li-O₂ cells with the aim of suppressing the side reactions activated by carbon material. Micro-particles of poly(3,4-ethylenedioxythiophene) (PEDOT), a conducting polymer, were used as the base material for the air electrode of Li-O₂ cells. The PEDOT micro-particles were treated with H₂SO₄ to improve their electronic conductivity, and LiBr and CsBr were used as the redox mediators to facilitate the dissociation of their action products in the electrode and reduce the over-potential of the Li-O₂ cells. The capacity of the electrode employing PEDOT micro-particles was significantly enhanced via H₂SO₄ treatment, which is attributed to the increased electronic conductivity. The considerable capacity enhancement and relatively low over-potential of the electrode employing H₂SO₄-treated PEDOT micro-particles indicate that the treated PEDOT micro-particles can act as reaction sites and provide storage space for the reaction products. The cyclic performance of the electrode employing H₂SO₄-treated PEDOT micro-particles was superior to that of a carbon electrode. The results of the Fourier-transform infrared spectroscopic analysis showed that the accumulation of residual reaction products during cycling was significantly reduced by introducing the carbon-free electrode based on H₂SO₄-treated PEDOT micro-particles, compared with that of the carbon electrode. The cycle life was improved owing to the effect of the redox mediators. Therefore, the use of the carbon-free electrode combined with redox mediators could realize excellent cyclic performance and low over-potential simultaneously.

Keywords : Lithium oxygen battery, Electrode, PEDOT, Micro-particle

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1. Introduction

Vehicles powered by internal combustion engines are being gradually replaced by eco-friendly electric vehicles powered by electric batteries because of environmental concerns. Li-ion batteries, which hold the largest share of the commercial market, are currently being employed in electric vehicles. The driving distance covered by electric vehicles is dependent upon the capacity of Li-ion batteries; thus, widespread research has been conducted to enhance the storage capacity of Li-ion batteries [1-5]. In spite of this endeavor, the short driving distance of electric

vehicles after a single charge remains a critical factor limiting their market share. Attempts to address these issues have led to the development of next-generation batteries as a possible alternative for Li-ion batteries. Particularly, Li-air batteries have a high theoretical energy density, similar to that of gasoline [6-10]; therefore, their use as batteries in electric vehicles can be expected to extend the driving distance. However, non-aqueous Li-air batteries present several major challenges such as high over-potential and limited cyclic performance [11-18].

Fundamentally, these challenges are related to the inherent nature and sluggish kinetics of the basic reaction between oxygen and lithium ions. An ideal basic reaction of a typical non-aqueous lithium-air (oxygen) cell is the formation of insoluble Li₂O₂ on the surface of

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the air electrode through the reduction of molecular oxygen and combination with lithium ions on discharging, and dissociation of this deposited material on charging. The slow kinetics during the dissociation process of Li_2O_2 results in the high over-potential. Efficient approaches to reduce the over-potential include the development of catalysts such as noble metals and transition metal oxides [19-25] for the air electrode, and the introduction of a redox mediator [26-32] dissolved in the electrolyte. However, the cyclic performance of lithium-air (oxygen) batteries is a more cumbersome hurdle because it is more strongly dependent upon the parasitic reaction on the surface of the air electrode than the ideal basic reaction [11-18]. Generally, insufficient cyclic performance is attributed to the clogging of the pores of the air electrode by the accumulated residual reaction products. Although the ideal reaction product, Li_2O_2 , is relatively easily dissociated, unwanted reaction products such as Li_2CO_3 and organic compounds ($\text{CH}_3\text{CO}_2\text{Li}$, HCO_2Li , etc.) derived from parasitic reactions hardly dissociate on charging, resulting in their accumulation on the surface of the air electrode [33-36]. Thus, the suppression of parasitic reactions on the air electrode is of key importance to obtain lithium-air (oxygen) cells with superior cyclic performance.

It is nettlesome that carbon, which is a widely used base material for an air electrode, activates the parasitic reaction during cycling [37-39]. Carbon is an almost irreplaceable material for an air electrode because of its high electronic conductivity, which compensates for the low conductivity of oxide catalysts and wide surface, thereby providing a large number of reaction sites and vast storage area for reaction products. However, carbon undergoes surface reactions with Li_2O_2 to form Li_2CO_3 , an unwanted reaction product, and this facilitates the decomposition of the electrolytes in the high potential range.

In this regard, in our previous work, conducting polymers such as poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), polyaniline, and poly(3,4-ethylenedioxythiophene) (PEDOT) micro flowers were suggested as possible base materials for an air electrode [40-42]. Conducting polymers are light materials and they exhibit considerable electronic conductivity; thus, they are expected to be possible candidates to substitute carbon in an air electrode. However, owing to their relatively low electronic conductivity compared with that of carbon materials, they have only been used as “composites”

with carbon as the base material of air electrodes. Therefore, our previous work using a conducting polymer suggested a polymer-covered carbon-based electrode rather than a carbon-free electrode.

In this study, an entirely carbon-free electrode based on a conducting polymer (PEDOT micro-particles) is introduced to suppress the parasitic reaction initiated by carbon materials. The relatively low electronic conductivity of PEDOT micro-particles is increased considerably by subjecting them to treatment with H_2SO_4 through a crystallization process [43] to obtain an air electrode consisting of pure polymer in the form of PEDOT micro-particles. Although carbon-free electrodes based on conducting inorganic materials such as TiC and Co_3O_4 have been reported [44-47], air electrodes based purely on polymeric materials have rarely been reported, to the best of our knowledge. In addition, redox mediators are merged with the air electrode containing H_2SO_4 -treated PEDOT micro-particles to reduce the over-potential and to efficiently dissociate the reaction products. The synergic effect of carbon-free air electrodes based on pure polymer and redox mediators is expected to deliver low over-potential and excellent cyclic performance.

2. Experimental

2.1 Synthesis of PEDOT micro-particles

EDOT monomer (Aldrich, 97%) was slowly dropped into a stirred AOT ternary solution, which was composed of the surfactant AOT (Aldrich, 96%), aqueous FeCl_3 (Aldrich, 97%) solution (7M), and p-xylene (Aldrich, anhydrous, $\geq 99\%$). This solution was continuously allowed to react at room temperature for 24 h and there after centrifuged with ethanol and deionized (DI) water until the supernatant was colorless and transparent. Finally, the residual product was dried under vacuum at 80°C for 24 h. Subsequently, the PEDOT powder was treated with 10 mL of sulfuric acid (Aldrich, 95-98%), stirred for 10 min, and washed several times with DI water through a vacuum filter. It was there after dried at 120°C for 8 h. X-ray diffraction (XRD) patterns of the PEDOT micro-particles were obtained using a Rigaku mini-flex II X-ray diffractometer with monochromatized Cu-K_α radiation ($\lambda = 1.5406 \text{ \AA}$).

2.2 Electrochemical tests

The electrodes employing pristine PEDOT micro-

particles were composed of 100% sample powder (without binder). As a standard sample, a carbon electrode was prepared by mixing 90 wt.% super P (as carbon) with 10 wt.% polyvinylidene fluoride (PVDF) binder. The loading weight of the electrodes was adjusted to $0.2 \text{ mg} \pm 0.02 \text{ mg}$. The electrochemical performance of the electrodes was examined using a modified Swagelok cell consisting of an air electrode, metallic Li anode, glass filter (Whatman) separator, and electrolyte containing 0.5 M LiTFSI and 0.5 M LiNO_3 in tetraethylene glycol dimethyl ether. A mixture of LiNO_3 with LiTFSI, a typical salt for Li-O_2 cells, was used because it can effectively stabilize the Li anode [28,32]. In addition, 0.05 M of LiBr and CsBr were used as dissolved catalysts (or redox mediators) in the electrolyte. The cells were assembled in an Ar-filled glove box and subjected to galvanostatic cycling using a WonATech battery cycler (WBCs 3000). The potential range was 2.0–4.35 V (vs. Li/Li^+) and the current density was $200 \text{ mA} \cdot \text{g}^{-1}$ for the electrochemical test. All the experiments were conducted in an ambient O_2 atmosphere.

2.3 Characterization of the electrode materials

Transmission electron microscopy (TEM, JEM-2100F (HR)) and scanning electron microscopy (SEM, Nova NanoSEM 450, FEI Co.) were employed to observe the shape of the PEDOT micro-particles. The sheet resistance of the PEDOT micro-particles was compared before and after treatment with sulfuric acid by preparing the samples as pellets and conducting the measurement using a four-point probe. The surface morphologies of the air electrodes before testing and after cycling were observed using SEM. In addition, Fourier-transform infrared spectroscopy (FTIR, Nicolet 5700, Thermo Electron Corp.) was used to examine the formation of Li_2O_2 and the amount of reaction products accumulated during cycling. Cycled specimens were prepared for SEM and FTIR analyses by collecting the air electrodes after 100 cycles and washing them in dimethyl carbonate several times, after which they were stored in a vacuum chamber for 24 h. The specimens were packed under vacuum and transferred to the instruments for measurement.

Fig. 1. SEM images (the left side) and XRD patterns (the right side) of the PEDOT micro-particles (a) pristine, (b) H_2SO_4 -treated.

3. Results and Discussion

Prior to the electrochemical test, the morphologies of the pristine and H_2SO_4 -treated PEDOT micro-particles were observed using SEM and XRD. As shown in Fig. 1a (the left side), the shapes of the pristine PEDOT micro-particles were characterized by sharp protrusions. In contrast, after H_2SO_4 treatment, the surfaces of the PEDOT micro-particles became relatively smooth. The XRD patterns in Fig. 1 (the right side) show that the crystallinity of the PEDOT micro-particles increased after H_2SO_4 treatment. The PEDOT micro-particles reportedly undergo structural rearrangement from amorphous to crystalline during H_2SO_4 treatment [43]. This structural rearrangement of PEDOT micro-particles leads to a morphological change as well. Moreover, it is inferred that the properties of the PEDOT micro-particles were also changed owing to the structural change.

To observe the effect of H_2SO_4 treatment, the electrochemical properties of the electrodes containing pristine and H_2SO_4 -treated PEDOT micro-particles were observed and compared using Li-O_2 cells. Fig. 2 shows the initial discharge-charge profile of the electrodes at a current density of $200 \text{ mA} \cdot \text{g}_{\text{electrode}}^{-1}$ in the voltage range 2.0–4.35 V. The initial capacity of the electrode employing pristine PEDOT micro-particles was only $\sim 500 \text{ mAh} \cdot \text{g}_{\text{electrode}}^{-1}$. However, the electrode employing H_2SO_4 -treated PEDOT micro-particles showed a stable discharge-charge profile under the limited capacity of $3000 \text{ mAh} \cdot \text{g}_{\text{electrode}}^{-1}$. This increased capacity is attributed to the enhanced conductivity of the PEDOT micro-particles owing to H_2SO_4 treatment. The resistances of the samples were compared by preparing pristine and H_2SO_4 -treated PEDOT micro-particles as pellets. The sheet resistance of the pellet containing pristine PEDOT micro-particles was $\sim 16.4 \Omega \cdot \text{sq}$, whereas that of the pellet containing H_2SO_4 -treated PEDOT micro-particles was $\sim 7.3 \Omega \cdot \text{sq}$. The morphological change observed in Fig. 1 could also affect the capacity of the electrode. Particularly, increasing the surface area of the sample can improve its capacity. However, the H_2SO_4 -treated PEDOT micro-particles with smooth surfaces may not have larger surface areas than pristine PEDOT micro-particles with sharp protrusions. Thus, the effect of the morphological change appears to be limited.

The considerable capacity of the electrode contain-

Fig. 2. Initial discharge-charge profiles of the electrodes containing (a) pristine PEDOT micro-particles, (b) H_2SO_4 -treated PEDOT micro-particles (current densities of $200 \text{ mA} \cdot \text{g}_{\text{electrode}}^{-1}$).

ing H_2SO_4 -treated PEDOT micro-particles shows that it is possible to realize a carbon-free electrode with sufficient capacity by using a conducting polymer. The over-potential appeared to be non-excessive compared with that of a typical electrode based on carbon. However, the over-potential was unsuitably high for use in a secondary battery with high efficiency. Thus, to reduce the over-potential of the Li-O_2 cells and ensure that the reaction product dissociated more efficiently, redox mediators (LiBr and CsBr) were added to the electrolyte. Generally, redox mediators (also known as dissolved catalysts) are directly oxidized at the electrode, followed by the oxidation of Li_2O_2 , whose reaction facilitates the dissociation of reaction products and reduces the over-potential of the cells. Moreover, the redox mediator dissolved in the electrolyte can easily establish con-

tact with solid reaction products to maximize the reaction area. LiBr, which contains bromide ions, has been suggested as a redox mediator with stable cyclic performance [26]. CsBr, which can dissociate into Cs^+ and Br^- ions, can act as a redox mediator at the air electrode (Br^-), whereas Cs^+ ions are expected to suppress dendrite growth at the Li anode [28,32].

Fig. 3 shows the initial discharge-charge profile of the electrode containing H_2SO_4 -treated PEDOT micro-particles. A standard carbon electrode composed of super P (90%) and PVDF binder (10%) was also prepared and examined to compare the electrochemical properties. As shown in Fig. 4a and 4b, the average voltage difference between the discharge and charge profiles of the carbon electrode was ~ 1.41 V, whereas that of the electrode containing H_2SO_4 -treated PEDOT micro-particles (without using a redox mediator) was only ~ 1.10 V. The low over-potential of the PEDOT electrode indicates that the PEDOT micro-particles can successfully act as reaction sites between lithium ions and oxygen. The good conductivity of the PEDOT surface suggests its suitability in terms of electron exchange for the formation and dissociation of reaction products such as

Li_2O_2 . The over-potential of the electrode employing H_2SO_4 -treated PEDOT micro-particles was further decreased when the redox mediators were introduced into the Li- O_2 cells. As shown in Fig. 3c and d, the use of redox mediators reduced the voltage difference between the discharge and charge profiles to 0.78-0.82 V. These results confirm that the introduction of redox mediators facilitates the dissociation of the reaction products.

Fig. 4 shows the cyclic performance and efficiency of the electrodes containing carbon and H_2SO_4 -treated PEDOT micro-particles at the current density of $200 \text{ mA} \cdot \text{g}_{\text{electrode}}^{-1}$. The cell capacity was set at $1000 \text{ mAh} \cdot \text{g}_{\text{electrode}}^{-1}$ to avoid a large depth of discharge [25]. The electrode containing carbon maintained a specified capacity up to 143 cycles, whereas the electrode employing H_2SO_4 -treated PEDOT micro-particles showed superior cycle life (263 cycles) with a specified capacity without using a redox mediator (Fig. 4a-b). The introduction of the redox mediators to the cells significantly enhanced the cyclic performance as shown in Fig. 4c-d. The cycle lives of the electrodes were 413 and 616 cycles for LiBr and CsBr, respectively. Notably, the intro-

Fig. 3. Initial discharge-charge profiles of the electrodes containing (a) super P (carbon) (b) H_2SO_4 -treated PEDOT micro-particles without redox mediator, (c) H_2SO_4 -treated PEDOT micro-particles with LiBr as the redox mediator, (d) H_2SO_4 -treated PEDOT micro-particles with CsBr as the redox mediator (current densities of $200 \text{ mA} \cdot \text{g}_{\text{electrode}}^{-1}$).

Fig. 4. Cyclic performance and efficiency of the electrodes containing (a) super P (carbon) (b) H_2SO_4 -treated PEDOT micro-particles without a redox mediator, (c) H_2SO_4 -treated PEDOT micro-particles with LiBr as the redox mediator, (d) H_2SO_4 -treated PEDOT micro-particles with CsBr as the redox mediator (capacities were set at $1000 \text{ mAh} \cdot \text{g}_{\text{electrode}}^{-1}$ and current densities at $200 \text{ mA} \cdot \text{g}_{\text{electrode}}^{-1}$).

duction of CsBr drastically increased the cycle life of the electrode. The cycle life of the Li- O_2 cells is critically affected by the accumulation of the reaction products during cycling. Electrolyte deficiency owing to the decomposition of the electrolyte during cycling can also limit the cycle life of the Li- O_2 cells. Moreover, an unstable Li anode may cause the cycle life of the Li- O_2 cells to deteriorate, especially during long cycles.

To elucidate the reason for the improved cyclic performance of the electrode containing H_2SO_4 -treated PEDOT micro-particles (with or without redox mediators), the electrodes were analyzed using FTIR spectroscopy, as shown in Fig. 5. The electrodes were collected after 100 cycles (in the charged state). As shown in Fig. 5a, the FTIR spectrum of the carbon electrode after 100 cycles presents several

Fig. 5. FTIR spectra of the electrodes containing (a) super P (carbon), (b) H_2SO_4 -treated PEDOT micro-particles without a redox mediator. The electrodes were cycled 100 times under the limited capacity of 1000^{-1} at the current density of $200 \text{ mA} \cdot \text{g}_{\text{electrode}}^{-1}$ (charged state).

distinct absorbance peaks, which represent the existence of large amounts of residual reaction products in the electrode. The intense broad peaks at $400\text{--}750$, $900\text{--}1100$, and $1350\text{--}1700 \text{ cm}^{-1}$ are attributed to undesirable reaction products such as $\text{CH}_3\text{CO}_2\text{Li}$ and Li_2CO_3 . This indicates that the limited cyclic performance of the carbon electrode is due to the accumulation of the undesirable reaction products derived from side reactions during cycling. In contrast, after 100 cycles, the FTIR spectrum of the PEDOT electrode (without redox mediators) showed much less intense absorbance peaks than those of the carbon electrode (Fig. 5b). This indicates that the accumulation of undesirable reaction products is significantly reduced by introducing H_2SO_4 -treated PEDOT micro-particles as the base material of the electrode instead of carbon. As mentioned before, the carbon material initiates side reactions; thus, a carbon-free electrode based on

Fig. 6. FTIR spectra of the electrodes containing (a) H_2SO_4 -treated PEDOT micro-particles with LiBr as the redox mediator, (b) H_2SO_4 -treated PEDOT micro-particles with CsBr as the redox mediator. The electrodes were cycled 100 times under the limited capacity of $1000 \text{ mAh} \cdot \text{g}_{\text{electrode}}^{-1}$ at the current density of $200 \text{ mA} \cdot \text{g}_{\text{electrode}}^{-1}$ (charged state).

H_2SO_4 -treated PEDOT micro-particles can suppress these side reactions and the accumulation of undesirable reaction products. This suppression results in the improved cyclic performance of the electrode containing H_2SO_4 -treated PEDOT micro-particles.

Fig. 6 shows the FTIR spectra of the electrode containing H_2SO_4 -treated PEDOT micro-particles cycled 100 times using redox mediators (LiBr and CsBr). All the peaks in the spectra appear broad with reduced intensity, indicating that the amount of residual reaction products is much less than that in the case of the carbon electrode shown in Fig. 5a. The redox mediators reduce the over-potential of the Li-O_2 cells, which can also contribute to the suppression of side reactions. The formation of Li_2CO_3 and the decomposition of electrolyte are activated by

applying high voltage [37-39]. Thus, reduction of the over-potential decreases the voltage range in which the charging process occurs, which can suppress the side reactions. Suppression of the side reaction by the redox mediator not only reduces the accumulation of reaction products in the electrode, but also delays electrolyte depletion during cycling. This is because decomposition of the electrolyte, a typical side reaction, can also be suppressed by the redox mediator. Particularly, during long cycles, electrolyte depletion can be an important factor limiting the cycle life. Thus, the enhancement of cycle life by the redox mediator can be explained by the reduction of the residual reaction products and delayed electrolyte depletion. However, it is difficult to explain the superior cyclic performance of the cell obtained when using CsBr rather than LiBr.

As shown in Fig. 4, the cycle life of the PEDOT electrode was significantly enhanced by the introduction of CsBr as a redox mediator even when compared with the use of LiBr. However, the redox mediators responsible for decomposing the reaction products, irrespective of whether CsBr or LiBr is used, all contain Br^- ions. Thus, the effect of CsBr cannot explain the effect of only using the redox mediator. The reason for introducing Cs^+ ions was to reduce the dendrite growth at the Li anode. The effect of the Cs^+ ions of the CsBr redox mediator was confirmed from SEM images of the Li anode of the Li-O_2 cells obtained after 5 cycles for comparison purposes. Fig. 7a shows the SEM image of the Li anode acquired from cells in which the redox mediator was not used (the electrode material was H_2SO_4 -treated PEDOT micro-particles). The surface appears to be very rough, and deep wrinkles and curvature are observed. The roughness of this surface was not lessened by using the LiBr redox mediator, as shown in Fig. 7b. However, when CsBr was used as the redox mediator, the surface of the Li anode changed dramatically. The deep wrinkles and curvature are no longer visible in the SEM images (Fig. 7c), and the surface appears to be very smooth, indicating that the Cs^+ ions successfully suppress dendrite growth. This result indicates that the cell in which the CsBr redox mediator is employed may have a more stable Li anode than the other cells in which a general electrolyte or the LiBr redox mediator is employed, which also leads to excellent cyclic performance of the cell with the CsBr redox mediator.

Fig. 7. SEM images of the Li anodes after 5 cycles (a) without a redox mediator, (b) using LiBr as the redox mediator, and (c) using CsBr as the redox mediator.

4. Conclusions

In this study, H_2SO_4 -treated PEDOT micro-particles were introduced as the base material of an air electrode of Li-O_2 batteries. This approach is expected to suppress the side reactions initiated by carbon materials, which are generally used as the base material of air electrodes. The electronic conductivity of the PEDOT micro-particles was improved via H_2SO_4 treatment, which significantly increased the capacity of the electrode containing PEDOT micro-particles. The considerable capacity and relatively low over-potential of the electrode containing H_2SO_4 -treated PEDOT micro-particles indicate that PEDOT micro-particles can act as a catalytically active base material for the air electrode of Li-O_2 cells. The over-potential of the electrode was considerably reduced by the introduction of LiBr and CsBr as redox mediators because these two compounds facilitate the dissociation of reaction products in the electrode.

The cyclic performance of the electrode containing H_2SO_4 -treated PEDOT micro-particles was superior to that of the carbon electrode. Considering the result of the FTIR analysis, compared with the case in which carbon was used as the electrode material, the amount of residual reaction products during cycling was significantly reduced when H_2SO_4 -treated PEDOT micro-particles were used as the electrode material. The reduced amount of residual reaction products indicates that the carbon-free electrode based on the H_2SO_4 -treated PEDOT micro-particles successfully suppresses side reactions, thereby improving the cyclic performance of the cells. The cyclic performance was further improved when redox mediators were introduced. Specifically, the electrode containing H_2SO_4 -treated PEDOT micro-particles combined with the CsBr redox mediator showed excellent cyclic performance and low over-potential. This is because the Cs^+ ions stabilized the Li anode, and the Br^- ions acted as the redox mediator.

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