PREPARATION AND ANALYSES OF MnO₂/CARBON COMPOSITES FOR RECHARGEABLE LITHIUM-AIR BATTERY

Ku-Bong Chung, Ju-Kyung Shin, Tae-Young Jang, Dong-Kyun Noh, Yongsug Tak and Sung-Hyeon Baeck

Department of Chemical Engineering, Inha University, 253 Yonghyun-dong, Nam-gu, Incheon 402-751, Korea

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Abstract. MnO₂-carbon composites with various Mn/C ratios were prepared by precipitation method. The composites were cast onto Ni foam to be evaluated as cathodes of Li-air battery. Charge-discharge tests were carried out by using a Swagelok type cell in an 1 M LiPF₆ in a mixture of propylene carbonate (PC), ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1:2 weight ratio). The influence of Mn/C ratio on both capacity and charge/discharge behavior was investigated. The cycle performance of Li/O₂ batteries was strongly dependent on Mn/C ratio. With increasing amount of MnO₂, the cycle performance of Li/O₂ batteries improved. The influence of electrolyte amount was also investigated, and the best cycle performance was achieved when 90 µL of electrolyte was used.

1. INTRODUCTION

There is a growing interest in smaller and lighter batteries to meet energy and environmental challenges. Rechargeable Li-air batteries have been considered as promising and realistic contenders for various applications [1–5]. The most characteristic feature of lithium metal–air batteries is that a tremendous amount of energy can be theoretically stored. In terms of specific capacity, lithium metal exhibits 1.3×10⁴ Whkg⁻¹, and the combination of lithium and air can achieve 1.1×10⁴ Whkg⁻¹ without considering the weight of oxygen (5.2×10³ Whkg⁻¹ with considering oxygen weight) [1–5]. The theoretical capacity of Li-air battery is 10 times higher than that of lithium-ion batteries, and this step-change in capacity will be able to pave the way for a new generation of electric cars, mobile phones and laptops.

In lithium-air batteries, non-aqueous electrolytes should be used for the anode to eliminate the reaction between metallic lithium and water. Abraham and Jiang [5] reported a Li-air battery using a non-aqueous electrolyte, and they suggested that lithium peroxide is a discharge product, based on 2Li + O₂ → Li₂O₂ (theoretical voltage of 3.10 V vs. Li⁺/Li). Due to low oxygen solubility in a non-aqueous electrolyte, however, the power density of a Li-air battery using a non-aqueous electrolyte is generally low [6,7]. Dobley et al. [8] and Kuboki et al. [9] also employed liquid organic solvents or ionic liquid-based electrolyte solution for the electrolyte, and reported that the products of the discharge was insoluble Li₂O and/or Li₂O₃, which could be precipitated in the pores of carbon based air electrode. Recently, a lithium-air rechargeable battery using MnO₂ as an air electrode has been reported [4]. However, cycle stability is not good, and further improvement in catalytic activity for the air electrode is required.

In this study, MnO₂-carbon composites with various Mn/C ratios were prepared, and they were used...
as catalysts of air electrodes in Li-air cell. Charge-discharge behavior and capacity with respect to Mn/C ratio was investigated using a Swagelok type cell in an 1 M LiPF₆ in a mixture of propylene carbonate (PC), ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1:2 weight ratio). The influence of electrolyte amounts on both capacity and charge/discharge behavior was also studied.

2. EXPERIMENTAL DETAILS

MnO₂/KB carbon composites with various Mn/C ratios were synthesized by a precipitation method using potassium permanganate (KMnO₄) as a precursor. Before synthesis, Ketjen black carbon (EC600JD, Akzo Nobel) was pretreated in an acidic solution (aqua regia) for 72 h, which was followed by washing in distilled water several times. Appropriate amounts of KMnO₄ aqueous solution were then added dropwisely into the carbon suspension. The Mn/C ratio was controlled by varying the concentration of potassium permanganate (KMnO₄) in the solution, and proper amount of ethanol was used as a reducing agent. After washing the resultant product in warm distilled water several times, it was dried in an oven at 100 °C overnight.

All of the synthesized samples underwent detailed analyses. The crystallinity of the synthesized samples was investigated by X-ray diffraction analysis (XRD; Rigaku, D/max-2200), and the oxidation states of the manganese were determined by X-ray photoelectron spectroscopy (XPS; Thermo-scientific, ESCA 2000). Transmission electron microscope (TEM) was utilized to examine the surface morphology. Surface area of synthesized catalyst was determined by Brunauer-Emmett-Teller (BET) measurement, and Mn/C ratio was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

A Swagelok-type cell, similar to the one reported by Beattie et al. [10], was used for the measurement of capacity. It was assembled in an argon-filled glove box with less than 1 ppm of moisture and oxygen concentration. A lithium metal (Sigma Aldrich, 0.38 mm thickness) was used as an anode, and an 1M LiPF₆ in a mixture of propylene carbonate (PC), ethylene carbonate (EC) and diethyl carbonate (DEC) with a weight ratio 1:1:2 was used as an electrolyte. The electrolyte was impregnated into a glass fiber separator (Whatman, GF/D). A mixture of synthesized MnO₂-carbon composites and PVdF binder (polyvinylidene fluoride, Alfa Aesar) with a weight ratio 95:5 was cast onto a nickel foam. After drying at 100 °C for 3 hours, it was employed as a air cathode. During discharge, O₂ pressure was kept to 1.2 atm to avoid contamination with humidity. The charge-discharge behavior was measured using a Potentiostat/Galvanostat (Princeton Applied Research, VSP) between 2.0 V and 4.5 V vs. Li⁺/Li⁺.

3. RESULTS AND DISCUSSION

The XRD patterns of the synthesized composite (the composite of 15 wt.%-MnO₂ and carbon) are shown in Fig. 1a. Broad peaks around 25° and 44° were assigned as halo patterns of Ketjen black. Two peaks around 37° and 66° were observed for all the synthesized samples, and they can be assigned as the characteristic peaks of manganese oxide [11]. The oxidation states of the manganese were determined by X-ray photoelectron spectroscopy, and Fig. 1b shows the XPS spectra of Mn 2p. All peaks were calibrated using the peak at 284.9 eV of adventitious carbon. The Mn 2p3/2 peak and Mn 2p1/2 observed at 642.1 eV and 653.5 eV, indicate that manganese...
mainly exists as $\text{Mn}^{4+}$ in $\text{MnO}_2$ [12]. It was clearly observed from XRD and XPS analyses that $\text{MnO}_2$. Carbon composites were successfully synthesized by a precipitation method.

To investigate surface morphology, transmission electron microscopy (TEM) analyses were carried out, shown in Fig. 2. The particles of Ketjen black carbon and manganese oxide were clearly observed; Ketjen black showed the sphere-like shape (Fig. 2a), while manganese oxide exhibited rod-like structure with $5 \sim 10$ nm diameter and $50 \sim 300$ nm length (Fig. 2b). $\text{MnO}_2$ nanorods were observed to be dispersed uniformly on the carbon surface. The Mn/C ratio was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and the results are summarized in Table 1. The Mn/C ratio in the samples was correlated remarkably well to the Mn/C ratio in the precursor, indicating that the catalyst composition can be controlled by varying the concentration of each component in the solution. Surface area of synthesized catalyst was determined by Brunauer-Emmett-Teller (BET) method, and they are also listed in Table 1. Ketjen black itself showed a very high surface area of 1423 m$^2$/g, and the surface area of synthesized catalysts decreased with increase of manganese oxide amount because of the relatively low surface area of $\text{MnO}_2$.

In Li-air battery, electrolyte has been known to play a very important role in dissolving oxygen and transporting lithium ion [13]. Different amount of electrolyte (1 M LiPF$_6$ in an 1:1:2 mixture of PC, EC, and DEC) was used, and the influence of electrolyte amount was investigated. Fig. 3 shows the initial discharge capacities of Li-air batteries with respect to electrolyte amount, and Fig. 4 shows cycle performance using the composite of 15 wt.%-$\text{MnO}_2$ and carbon as an air electrode. With increasing amounts of electrolyte, the initial discharge capacity increased significantly, while cycle performance of Li/O$_2$ batteries became worse. A volume expansion was reported after soaking air electrode with electrolyte [14], resulting in the increase of porosity, which can facilitate the formation of tri-phase region (electrolyte-catalyst-oxygen). The increase of initial discharge capacity with electrolyte amount can be attributed to the facilitated formation of tri-phase region. However, more solid products ($\text{Li}_2\text{O}_2$, $\text{Li}_2\text{O}$, $\text{Li}_2\text{CO}_3$) can be deposited onto the air electrode surface during discharge with increase of electrolyte amount, resulting in increase of charge po-

Table 1. $\text{MnO}_2$ content measured by ICP-AES and BET surface area as a function of Mn content (wt.%). Specific surface area of synthesized catalyst was determined by Brunauer-Emmett-Teller (BET) method.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\text{MnO}_2$ Content (%)</th>
<th>Specific surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KB carbon</td>
<td>-</td>
<td>1423</td>
</tr>
<tr>
<td>5 wt.%-$\text{MnO}_2$ and carbon</td>
<td>4.9</td>
<td>1277</td>
</tr>
<tr>
<td>10 wt.%-$\text{MnO}_2$ and carbon</td>
<td>9.8</td>
<td>1185</td>
</tr>
<tr>
<td>15 wt.%-$\text{MnO}_2$ and carbon</td>
<td>13.6</td>
<td>1118</td>
</tr>
</tbody>
</table>
Fig. 4. Cycle performance with respect to electrolyte amount. The composite of 15 wt.%-MnO_2 and carbon was used for the air electrode.

Fig. 5. Cycle performance with respect to Mn content. 90 μL of electrolyte (1 M LiPF_6 in an 1:1:2 mixture of PC, EC and DEC) was used.

Fig. 6. Charge-discharge behavior of the composite of 15 wt.%-MnO_2 and carbon.

From the above results, it can be concluded both the surface area and the amount of catalyst are the key factors to be considered in designing air electrode.

4. CONCLUSIONS

MnO_2-carbon composites with various Mn/C ratios were successfully prepared by a precipitation method after pretreatment of Ketjen black carbon in an acidic solution. MnO_2 particles on a nano scale were finely dispersed on the surface of carbon, and the Mn/C ratio in the samples was easily controlled by varying the concentration of each component in the solution. The electrochemical properties of the synthesized samples were evaluated by both capacity and charge/discharge behavior in Li-air batteries. The cycle performance of Li-air battery is strongly dependent on both amount of electrolyte and Mn/C ratio. With increasing MnO_2 content, the...
cycle performance of Li-air battery was enhanced. Among all samples tested, the composite of 15 wt.%-MnO$_2$ and carbon showed the highest cycle performance for a Li-air cell.

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**REFERENCES**