Characterization of the Discharge Reaction Products in the Aqueous Li/O₂ Cell

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Introduction

Electrochemical energy storage devices such as rechargeable batteries are key components for innovative power train systems such as HV, PHV, FCHV and EV. Especially for the long range PHV and EV, the energy density of the battery system is very critical. Since current Li-ion batteries do not provide enough energy density for long range PHV or EV, R&D activities for post Li-ion batteries are getting more active all over the world.

 Li/O_2 battery is one of the most expected post Li-ion battery systems, because of its high theoretical energy density comparable with ICE [1]. Most of the groups are working on the non-aqueous Li/O_2 battery system whose discharge reaction is described in the equation (1). [2, 3]

$$2\mathrm{Li}^{+} + \mathrm{O}_{2} + 2\mathrm{e} \rightarrow \mathrm{Li}_{2}\mathrm{O}_{2} \tag{1}$$

In spite of the lower theoretical energy density, our group has been focusing on an aqueous Li / O_2 battery system based on the reaction (2), because overpotential of the charge-discharge reaction is much lower than that of the non-aqueous system. [4, 5]

$$4Li^{+}+O_2 + 2H_2O + 4e \rightarrow 4LiOH$$
 (2)

Based on the aqueous system, we have previously reported the electrochemical behavior of the aqueous Li / O_2 cell, however the actual electrochemical reaction has never been confirmed.

In the present study, the reaction products of the aircathode during the discharging process was investigated using XRD and Raman spectroscopy, and discussed the actual electrochemical reaction of the aqueous Li / O_2 cell.

Experimental

A gas diffusion electrode used in this study consists of two layers of carbon based electrode layer. As a reaction layer of the electrode, Ketjen black and PTFE was mixed in the mortar and pestle and pressed into a uniform sheet. The prepared sheet was punched and layered with a carbon paper used as a diffusion layer.

A specially designed Li/O_2 cell was fabricated using the gas diffusion electrode as the cathode, a lithium foil as the anode and a lithium conducting glass ceramics (OHARA) as the separator of the aqueous / non-aqueous electrolyte solution. The fabricated cell was placed into a chamber filled with pure oxygen. Galvanostatic discharge reaction was performed under various conditions.

After the discharging reaction, the Li/O_2 cell was immediately disassembled in an N₂ filled glove bag and the electrode was rinsed with dry ethanol. Then the obtained electrode was analyzed with XRD and Raman spectroscopy.

Results and Discussion

Figure 1 shows a series of XRD patterns for discharged electrodes compiled with simulated XRD

patterns for Li₂CO₃, LiOH•H₂O and Li₂O₂. Surprisingly all the samples had Li₂O₂ as the main reaction product during the discharging process. Slight amount of LiOH•H₂O was detected as well. This result suggests that the actual discharge product is Li₂O₂, which is same discharge product as the non-aqueous system, and then the Li₂O₂ was partially hydrolyzed into LiOH•H₂O (3).

$$Li_2O_2 + 3H_2O \rightarrow 2LiOH \bullet H_2O + 1/2O_2 \uparrow (3)$$

This result suggests that an effective catalyst need to be developed to minimize the energy loss of the two-step reaction. In addition, further analytical results will be discussed in the presentation.



Figure 1. XRD Patterns of the discharged cathodes in the $\rm Li/O_2$ cell compiled with the simulated diffraction patterns

Reference

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