Oxygen concentration measurement in the porous cathode of a lithium-air battery using a fine optical fiber sensor

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Abstract
The oxygen concentration distribution in the porous cathode of a lithium–air battery during discharge has been measured using a fine optical fiber sensor. The lithium–air battery has the highest theoretical capacity. However, for practical application, the lithium–air battery power density needs to be improved. To realize a more powerful aqueous lithium–air battery, sufficient oxygen supply into the porous cathode is required. No previous studies have measured the oxygen concentration in the porous cathode structure. In this study, platinum tetrakis pentafluorophenyl porphine (PtTFPP) was used as the oxygen indicator. When PtTFPP is exposed to excitation light, phosphorescence emission occurs, and its intensity depends on the oxygen partial pressure. Thus, the oxygen concentration can be obtained by measuring the phosphorescence intensity and using calibration data. A fine optical fiber sensor (110 μm in diameter) was constructed with PtTFPP painted on the edge. According to the experimental results, as the current density increases, the oxygen concentration in the porous cathode drastically decreases. Because of slow oxygen transport in the aqueous electrolyte and the existence of an electrolyte between the air layer and the porous cathode, sufficient oxygen is not supplied to the porous cathode. Therefore, only oxygen near the electrode surface can contribute to the discharge.

Keywords: Lithium–air battery, Porous cathode, Oxygen concentration, Optical measurement, Fiber sensor

1. Introduction

In recent years, energy and environmental problems have attracted great attention, and consequently electric vehicles are becoming one of the solutions. However, current lithium–ion batteries have a small electric capacity and it is difficult to extend the cruising distance of electric vehicles with lithium-ion batteries. In addition, the electrolyte in lithium–ion batteries has ignitability in air. Therefore, development of a secondary battery with higher energy density and safety is required.

The lithium–air battery has the highest theoretical capacity. Aqueous lithium–air batteries use an aqueous electrolyte without ignitability and oxygen as the active material of the cathode. Therefore, the aqueous electrolyte realizes cost reduction and ensures the safe use of the battery. Most of the battery structure can be composed of the anode, and a high theoretical energy density can be achieved (Girishkumar et al., 2010). In this study, we focus on the aqueous lithium–air secondary battery. The reaction in the cathode occurs by dissolution and diffusion of oxygen in the aqueous electrolyte, but insufficient oxygen supply from the air layer limits oxygen transport to the reaction site (Shibata et al., 2015). To realize a more powerful aqueous lithium–air battery, it is necessary to clarify and improve the oxygen transport phenomena in the porous cathode. However, no studies have measured the oxygen concentration in the porous cathode. In this study, we developed a technique to measure the oxygen concentration in the porous cathode under operating conditions by inserting a fine optical fiber oxygen sensor.
2. Experiment

2.1 Method for measurement of the oxygen concentration

Platinum tetrakis pentfluorophenyl porphine (PtTFPP) was used as the oxygen indicator (Chu and Lin, 2014). When PtTFPP is exposed to excitation light ($\lambda = 405$ nm), phosphorescence emission ($\lambda = 650$ nm) is produced, and its intensity depends on the oxygen partial pressure. Thus, the oxygen concentration can be obtained by measuring the phosphorescence intensity and using calibration data. PtTFPP was painted on the edge of an optical fiber with a diameter of 110 $\mu$m. To measure the phosphorescence intensity, bifurcated optical fibers were connected to the excitation light source and spectrometer. The phosphorescence intensity changes for different oxygen concentrations are shown in Fig. 1. The phosphorescence intensity change at 650 nm depended on the oxygen concentration.

Fig. 1 Phosphorescence intensity changes at different oxygen concentrations.

To convert the phosphorescence intensity to the oxygen concentration, we used the Stern–Volmer equation (Chu and Lin, 2014, Lakowicz, 1999):

$$\frac{I_0}{I} = 1 + A \cdot [O_2]$$  \hspace{1cm} (1)

where $I$ is phosphorescence intensity, $I_0$ is phosphorescence intensity without oxygen, $[O_2]$ is the oxygen concentration, and $A$ is a constant determined for the experiment. In this study, $I_0$ obtained by the calibration experiment without oxygen was 1.42, and $A$ obtained when $I$ was 1.0 and $[O_2]$ was 7.92 g/m$^3$ in the initial state was 0.053.

The measurement uncertainty was evaluated as follows (BIPM et al., 2008). The standard measurement uncertainty of the intensity from the light source and the sensitivity of the spectrometer, obtained by the intensity measurement results excluding phosphorescence intensity at the time of open circuit, was 0.089%. The standard measurement uncertainty of the phosphorescence intensity, obtained by the experimental results at the time of open circuit, was 0.12%. Therefore, the combined standard measurement uncertainty was 0.15%, and the expanded measurement uncertainty was 0.3%. The expanded measurement uncertainty was obtained by multiplying the combined standard measurement uncertainty by a coverage factor $k = 2$. Taking $k = 2$, the combined standard measurement uncertainty has a normal distribution, and the expanded measurement uncertainty produces permissible tolerance having a confidence level of approximately 95%.

2.2 Experimental setup and procedure

The experimental setup is shown in Fig. 2. The porous cathode (SIGRACET 10AA, SGL Group, USA) was horizontally fixed near the electrolyte interface. Thus, the porous cathode was soaked in the aqueous electrolyte. The structure of the porous cathode is a carbon fiber aggregate. A scanning electron microscopy image of the porous cathode is shown in Fig. 2. The fine optical fiber sensor was placed under the cathode in the electrolyte, moved up, and inserted into the cathode. To measure the phosphorescence intensity, bifurcated optical fibers were connected to the excitation light source and spectrometer. From the start of discharge, the phosphorescence intensity was measured at arbitrary positions in the porous cathode. The composite anode was water stable and had a multilayer structure for the
aqueous lithium–air battery (Zhang et al., 2008).

The conditions for measurement of the oxygen concentration are given in Table 1. The fine optical fiber sensor was fixed to the fine adjusting device and the initial position under the porous cathode \( (z = 0 \, \mu m) \) was arbitrary defined (Fig. 2). The fiber adjusting device was used as the sensor support and could traverse slightly in the vertical direction. The sensor was moved up in 70 \( \mu m \) increments and the oxygen concentrations of both inside and outside the porous cathode were measured (total of 15 points).

The electrochemical experimental conditions are given in Table 2. At each height, a discharge test was performed according to the protocol given in Table 2 and the time change of the oxygen concentration was measured at each current density. The fluorescence intensity before each discharge experiment was almost the same value. When the discharge experiment was completed and enough time passed, the fluorescence intensity returned to the initial value. In addition, the batteries showed approximately the same open circuit voltage before and after the discharge through the all experiment. Therefore, under the assumption that the discharge experiment is reproducible, the oxygen concentration at the same current density and time was plotted for each height. Finally, the spatial and temporal distribution of the oxygen concentration for each current density was obtained.

Fig. 2   Experimental setup.

| Parameter                               | Condition                        |
|-----------------------------------------|----------------------------------|
| Measurement interval (Exposure time)    | 5 sec                            |
| Movement range of optical fiber sensor  | 0–980 \( \mu m \)                |
| Resolution of movement range            | 70 \( \mu m \) (Total of 15 points) |

| Parameter     | Condition                                      |
|---------------|------------------------------------------------|
| Measurement time |                                                |
| 0–30 sec      | Open circuit                                   |
| 30–150 sec    | Constant current discharge \((0.05, 0.10, 0.15, 0.20 \, mA/cm^2)\) |
| 150–300 sec   | Open circuit                                   |

3. Results and discussion

The inverse phosphorescence intensity at one point in the porous cathode plotted against time is shown in Fig. 3. When discharge starts, the inverse phosphorescence intensity gradually decreases. In particular, when the current density increases, the rate of the change of the inverse phosphorescence intensity increases. After discharge, the inverse phosphorescence intensity gradually recovers and reaches the initial position because oxygen dissolved in air diffuses into the porous cathode. Therefore, we successfully measured the temporal change of the local oxygen concentration in the porous cathode.
Fig. 3  Inverse phosphorescence intensity at one point ($z = 350 \mu m$) in the porous cathode plotted against time.

The spatial and temporal oxygen concentration distribution at each current density is shown in Fig. 4. In this experiment, the oxygen concentration at 140–490 $\mu m$ greatly decreases, and the distance between both ends of the range (140–490 $\mu m$) is approximately equal to the thickness of the cathode (340 $\mu m$). Therefore, we successfully measured the decrease in the oxygen concentration in the porous cathode during discharge. On the other hand, oxygen concentration gradients are present at both ends of the lower side (0–140 $\mu m$) and upper side (490–910 $\mu m$) of the cathode. It is considered that the oxygen concentration recovers at the lower side (0–140 $\mu m$) of the cathode because oxygen is supplied from the dissolved oxygen in the electrolyte.

Fig. 4  Spatial and temporal oxygen concentration distributions on discharge at (a) 0.05, (b) 0.10, (c) 0.15, and (d) 0.20 mA/cm$^2$. The lower electrolyte layer is 0–140 $\mu m$. The porous cathode is 140–490 $\mu m$. The upper electrolyte layer is 490–910 $\mu m$. The air layer is 910–980 $\mu m$. 
When discharge starts, the oxygen concentration in the cathode gradually decreases it reaches almost zero at 0.15 mA/cm² or more. Therefore, these experimental results show the appropriate oxygen concentration distributions. Additionally, it is considered that the existence of the electrolyte between the air layer and the cathode inhibits oxygen transport from the air layer because the oxygen concentration greatly decreases in the electrolyte at the upper side of the cathode. To realize sufficient oxygen transport from the air layer, it is necessary to thin the electrolyte layer between the air layer and the cathode. However, it is difficult to make a thin electrolyte layer and successfully match the electrolyte surface and the edge of the electrode.

4. Conclusions

We have successfully measured the spatial and temporal distribution of the oxygen concentration using a fine optical fiber sensor. The fluxes at both sides of the cathode (upper and lower sides) are discussed and comprehensibly interpreted. The electrolyte layer that forms between the air layer and the cathode causes oxygen transport resistance. To realize sufficient oxygen transport from the air layer, it is necessary to thin the electrolyte layer between the air layer and the porous cathode.

References

BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML, Guide to the Expression of Uncertainty in Measurement JCGM 100:2008, GUM 1995 with minor corrections (online), available from <https://www.bipm.org>, (accessed on 5 May, 2019).

Chu, CS. and Lin, CA., Optical fiber sensor for dual sensing of temperature and oxygen based on PrTFPP/CF embedded in sol-gel matrix, Sensors and Actuators B: Chemical, Vol.195 (2014), pp.259–265.

Girishkumar, G., McCloskey, B., Luntz, A. C., Swanson, S., Wilcke, W., Lithium-Air Battery: Promise and Challenges, The Journal of Physical Chemistry Letters, Vol.1 (2010), pp.2193–2203.

Lakowicz, J.R., Principles of Fluorescence Spectroscopy (3rd ed.), Kluwer Academic/Plenum Press, New York (1999), Chapters 8.

Shibata, K., Uemura, S., Tsushima, S., Hirai, S., Reaction and Mass Transport Simulations by LBM in Electrolyte of Aqueous Lithium-Air Battery, The Electrochemical Society Transactions, Vol.64, No.19 (2015), pp.39–46.

Zhang, T., Imanishi, N., Hasegawa, S., Hirano, A., Xie, J., Takeda, Y., Yamamoto, O., Sammes, N., Li/Polymer Electrolyte/Water Stable Lithium-Conducting Glass Ceramics Composite for Lithium-Air Secondary Batteries with an Aqueous Electrolyte, Journal of the Electrochemical Society, Vol.155, No.12 (2008), pp.A965–A969.