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Short communication

Examination of graphene nanoplatelets as cathode materials for lithium–oxygen batteries by differential electrochemical mass spectrometry



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ABSTRACT

In this study, *in situ* differential electrochemical mass spectrometry was employed to investigate the electrochemical rechargeability of two types of graphene nanoplatelets (GNPs) as electrode materials for lithium–oxygen batteries by evaluating oxygen efficiency as well as coulombic efficiency. GNPs having hydrophobic surfaces exhibit much higher specific capacity than those having hydrophilic surfaces. When lithium nitrate–*N*,*N*dimethylacetamide (LiNO₃–DMAc) is used as the electrolyte, the lithium–oxygen battery exhibits a long cycle life, and unwanted side reactions are effectively suppressed. The LiNO₃–DMAc electrolyte is more stable than the lithium bis(trifluoromethane)sulfonamide–tetraethylene glycol dimethyl ether electrolyte, as evidenced by high O₂ evolution and low CO₂ evolution.

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1. Introduction

The lithium–oxygen $(Li-O_2)$ battery has attracted significant attention because, theoretically, it can achieve energy densities several times greater than those exhibited by current Li-ion batteries [1]. Despite the high energy density exhibited by this battery, some critical challenges need to be overcome with regard to its low round-trip efficiency, rate capability, and limited cycle life [2].

An ideal cathode for Li– O_2 batteries should possess many critical factors. Thus far, studies have been reported on the optimization of porous carbon to increase the effective oxygen diffusivity [3], selection of solvents with high oxygen solubility [4], and the use of fluorinated additives as oxygen carriers [5]. Especially, poor oxygen solubility and diffusivity in the electrolyte can restrict the kinetics of the cathode, which in turn can affect the overall performance of the electrochemical cell [6]. Insufficient oxygen input as well as the sluggish reduction of O_2 to electrochemically active oxygen species in the electrode, particularly at high current density, results in serious charge–discharge polarization and poor rate capability. Therefore, it is important to evaluate the moles of O_2 consumed or evolved during galvanostatic discharge–charge in Li– O_2 cells.

In recent studies, differential electrochemical mass spectrometry (DEMS) has been employed to determine the products obtained not only by electrolyte decomposition but also during battery charging [7, 8]. Thus far, most of the reported studies employing DEMS have quantified the ratio of O_2 consumed per electron during the cycling of cells

* Corresponding author. E-mail address: dwkim1@korea.ac.kr (D.-W. Kim). using different solvents. McCloskey et al. have extensively examined the stability of numerous solvents and salt combinations by DEMS [9, 10]. Despite a number of reported studies, the stability of the electrolyte in $\text{Li}-\text{O}_2$ cells still remains questionable.

Most of these previous studies have been conducted mainly using Super P, XC-72, and P50, types of carbon black, as the carbonaceous cathode. Until now, graphenes as cathode materials have received considerable attention for application in Li–O₂ batteries and have been widely investigated because of their large specific surface area as well as high electronic conductivity and electrocatalytic activity [11]. In this study, to better understand the electrochemistry of Li–O₂ batteries with graphene nanoplatelets (GNPs) as the electrode materials, for the first time, we combined *in situ* quantitative gas-phase mass spectrometry with DEMS. Additionally, comparative studies between different electrolytes are demonstrated, which provide the compatibility with GNP electrodes.

2. Materials and methods

Two types of commercial GNPs are denoted as GNP-1 (Product: N002-PDR, Angstron Materials Inc., USA) and GNP-2 (Product: xGnP®, XG Sciences, USA). For the preparation of carbon cathodes, an aqueous slurry of 70% GNPs and 30% carboxymethyl cellulose was cast on a nickel mesh. A loading mass of the graphenes was approximately 0.15 mg cm⁻². The electrolytes used in the lithium air cell were prepared by dissolving either lithium nitrate (LiNO₃) or lithium bis(trifluoromethane)sulfonamide (LiTFSI) in *N*,*N*-dimethylacetamide (DMAc) or Tetraethylene glycol dimethyl ether (TEGDME) at a concentration of 1 M.

Galvanostatic electrochemical measurements were conducted in Swagelok®-type cells containing a lithium metal anode, a GNP cathode, and a separator soaked with an electrolyte. A custom-made *in situ* DEMS system was constructed, similar to the IBM setup reported in the literature [10]. Oxygen efficiency, η_{O2} , is defined by the following equation; $\eta_{O2} = \Delta n_{ch} / \Delta n_{disch}$, where Δn_{ch} and Δn_{disch} are the oxygen amount evolved during charge and consumed on discharge, respectively.

3. Results and discussion

To investigate the catalytic effect of GNPs on the electrochemical properties of $\text{Li}-O_2$ batteries, air electrodes were prepared and tested between 2.2 and 4.4 V at a current density of 300 mA g⁻¹. The charge–discharge profiles of both GNP-1 and GNP-2 at the first cycle are compared in Fig. 1. Initially, a high discharge capacity of 11,400 mAh g⁻¹ is observed for the GNP-1 electrode, which is close to that reported previously [12]. This initial discharge capacity is 40 times larger than that exhibited by the GNP-2 electrode (287 mAh g⁻¹). Furthermore, it is obvious that the polarization of the GNP-1 electrode is lower than that of the GNP-2 electrode, as shown in the inset of Fig. 1.

The electrochemical performance of the GNP cathodes was investigated in Li-O₂ cells using LiNO₃-DMAc as the electrolyte at a current density of 200 mA g^{-1} , as shown in Fig. 2(a). GNP-1 is discharged– charged at a fixed capacity of 1000 mAh g⁻¹. Both GNP-1 and GNP-2 exhibit similar electrochemical potential despite the obvious difference in specific capacity. To probe discharge-charge reactions in more detail, in situ DEMS was conducted, as shown in Fig. 2(b). DEMS data clarify that there is substantial difference in the oxygen efficiency between the two GNP cathodes. GNP-1 electrode exhibits much higher oxygen efficiency than GNP-2 (77% vs 15%). Given the reaction of $2(\text{Li}^+ + \text{e}^-) + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$, theoretical ratio of electrons passed per oxygen molecules (e^{-}/O_{2}) would be 2.0. The e^{-}/O_{2} of GNP-1 on charge is 2.91, which is much closer to the ideal value than 16.11 of GNP-2. The much higher oxygen efficiency and close-to-ideal e^{-/}O₂ of GNP-1 elucidates that GNP-1 is more stable during discharge-charge cycles and more desirable cathode material than GNP-2.

Importantly, these differences of the oxygen efficiency and Li-O₂ battery performance of two GNPs can be associated with the differences of physical properties between GNP-1 and GNP-2, for example, surface area, porosity, and hydrophilicity (or hydrophobicity). Bruce et al. [13] mentioned that carbon with a hydrophobic surface is more stable and



Fig. 1. Voltage profiles of Li–O₂ batteries using LiNO₃–DMAc as the electrolyte and GNP electrodes cycled at a current density of 300 mA g^{-1} in the first cycle. The inset shows the enlarged voltage profiles of each electrode at initial regions.

exhibits lower electrolyte decomposition than that of carbon with a hydrophilic surface. Similarly, the GNP-1 here exhibits the relatively hydrophobic surface characteristic compared to the GNP-2 (inset of Fig. 2(a)). Therefore, it could be believed that little or no decomposition of electrolyte occurs on the hydrophobic carbon (GNP-1) and marginal decomposition of electrolyte occurs for hydrophilic carbon (GNP-2). Also, we examined the specific surface areas and pore-size distributions of the GNP-1 and GNP-2 electrode. The surface area of GNP-1 was 504.3 $m^2 g^{-1}$, as measured by the BET method; the GNP-2 was 672.5 m² g⁻¹. The pore volume of GNP-1 was 2.2 cm³ g⁻¹, as measured by the BJH method; the GNP-2 was $0.9 \text{ cm}^3 \text{ g}^{-1}$. As mentioned by Tran et al. [3], the discharge performance depends on the pore volume. Therefore, we confirmed that GNP-1 electrode material is appropriate for Li-O₂ battery and extremely high capacity is attributed to the enhancement of oxygen transport, caused by an increase in the number of inner large micropores.

Fig. 3(a) shows the discharge-charge curves of GNP-1 electrode using LiNO₃-DMAc and LiTFSI-TEGDME as the electrolytes at a current density of 200 mA g⁻¹, which are discharged to a specific capacity of 1000 mAh g⁻¹ with subsequent charging to a voltage limit of 4.4 V. Both electrolytes show different discharge-charge patterns. The charge potential of the GNP-1 electrode in the LiNO₃-DMAc electrolyte is less than that in the LiTFSI-TEGDME electrolyte. During the charging process, the LiNO₃-DMAc-containing cell maintains a potential of approximately ~3.5 V and then increases to higher potentials (3.7–4.4 V). However, the LiTFSI-TEGDME-containing cell exhibits a very brief plateau at ~3.2 V and then increases to higher potentials (4.3–4.4 V). The charge potential of the LiNO₃-DMAc-containing cell is constantly lower than that of the LiTFSI-TEGDME-containing cell, and it is suitable for application in Li–O₂ batteries.

To probe the reactions on discharge in more detail, especially electrolyte stability, in situ DEMS experiment was also employed. DEMS results of cells using LiNO₃-DMAc and LiTFSI-TEGDME as the electrolytes are shown in Fig. 3(b). Both electrolytes exhibit similar rate and quantity in the oxygen consumption during discharge comparable to the theoretical value of 2.0 for pure Li_2O_2 (2.23 e⁻/O₂ of DMAc vs 2.22 of TEGDME), implying that they have similar Li₂O₂ yields. However, more disparities are observed with respect to the quantity of O_2 gas on the subsequent charging process. The oxygen efficiency of the DMAc-containing cell is 77%, whereas the ratio of TEGDME-containing cell corresponds to 42%. For Li-O₂ batteries, an ether has been considered as a preferred choice of electrolyte solvent due to stability and primary formation of Li₂O₂ [14]. However, low current efficiency for O₂ release has been observed during charge by *in situ* gas analysis. Thus, the DMAc-containing cell exhibits better electrochemical rechargeability than that of the TEGDME-containing cell.

To further investigate the charging process, O₂, CO₂, and H₂ gases were evaluated by DEMS, as shown in Fig. 3(c). We focused on CO₂ as the main decomposition product and O₂, which were detected in situ using a mass spectrometer with the flow of argon as the carrier gas. Parallel to the beginning of the charging step at 1000 mAh g^{-1} , a strong increase in the ion current for O_2 (m/z = 32) is observed, accompanied by a minor increase in the ion current for CO_2 (m/z = 44) and H₂ (m/z = 2). Using the LiNO₃-DMAc electrolyte, a strong evolution of O₂ gas is detected during the whole charging plateau below 4.0 V, while signal of CO₂ suddenly increase after 4.0 V. The evolution of H₂ gas is undetected. However, the major gas evolved is O₂ with a relatively small amount of CO₂ and H₂ during the charging process using the LiTFSI-TEGDME electrolyte. The O₂ evolution profile occurs in two steps, and relatively, the amount of CO₂ is evolved near the end of the charging process caused by carbon corrosion [14]. The release of CO₂ and a high OER potential during the charging and discharge processes are influenced by electrolyte decomposition or oxidation [15]. As discussed elsewhere, CO₂ evolution during the charging process is due to the decomposition of deposits of solid carbonate formed at the interfaces of C-Li₂O₂ and Li₂O₂-electrolytes, and an

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