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Discharge product morphology versus operating temperature in non-aqueous lithium-air batteries

P. Tan, W. Shyy, T.S. Zhao[*], Z.H. Wei, L. An

Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR, China

H I G H L I G H T S

- The effect of the operating temperature on the product morphology is investigated.
- The product shape does not vary with temperature, but changes with current density.
- The product size decreases with an increase in the operating temperature.
- The operating temperature affects the capacity, charge voltage, and cyclability.

A R T I C L E I N F O

A B S T R A C T

During the discharge process of non-aqueous lithium-air batteries, a solid product, Li_2O_2, forms in the pores of the porous cathode, and eventually causes the discharge process to cease. During the charge process, solid Li_2O_2 needs to be electrochemically oxidized. The morphology of the discharge product is, therefore, critically related to the capacity and reversibility of the battery. In this work, we experimentally show that for a given design of the cathode, the shape of the discharge product Li_2O_2 at a given discharge current density remains almost unchanged with a change in the operating temperature, but the size decreases with an increase in the temperature. We also demonstrate that the product shape varies with the discharge current density at a given temperature. The practical implication of these findings is that the capacity, charge voltage, and cyclability of a given non-aqueous lithium-air battery are affected by the operating temperature.

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1. Introduction

Non-aqueous lithium-air batteries have been considered as one of the most promising power sources for electric vehicles and portable devices [1], primarily due to the high theoretical capacity (3.86×10^3 mAh g^{-1}) and high voltage (2.96 V), which corresponds to the energy density of 1.14×10^4 Wh kg^{-1} of lithium metal. Even based on the consideration of the entire battery system, the capacity of non-aqueous lithium-air batteries is still several times higher than that of Li-ion batteries [2–5]. Before this technology can be commercialized, however, a number of hurdles must be overcome, including the instability of electrolyte and electrode materials [6–9], significantly lower than theoretical discharge capacity attainable in the present time [10], poor operational

reversibility [11], and low energy efficiency [12].

The reasons of these issues are as follows: during discharge, active intermediates are produced, such as O_2^- and O_2^{2-} [13,14], which may decompose the non-aqueous electrolyte [6–8], the porous cathode [9], and even the current collector [15], leading to the instability of materials. The discharge product, Li_2O_2 [16,17], is insoluble in the non-aqueous electrolyte and grows in the pores of the porous cathode with an increase in the capacity [18]. The grown product can eventually impede the contact among oxygen, lithium ions, and electrons [19], terminating the discharge process and leading to a lower utilization of the cathode, thus resulting in a lower actual discharge capacity [20–22]. During charge, side products (e.g. Li_2CO_3) can cause a large overpotential and lead to the low energy efficiency and poor reversibility [23]. In addition to side products, the charge voltage can also be significantly affected by the morphology of Li_2O_2 [24–26]. Small-sized product particles lead to the low average voltage of charge plateaus, while large-

sized product particles can result in a high charge plateau [25,26]. Such a high voltage can not only affect the energy efficiency, but also aggravate side reactions (e.g. decomposition of carbon at the voltage larger than 3.5 V) [9], thus contributing to the poor reversibility. The morphology of the discharge product is, therefore, critically related to the capacity and reversibility of the battery.

The toroid-like morphology of Li_2O_2 was reported in various electrode and electrolyte systems [27–32]. In addition, the film-like Li_2O_2 on glassy carbon was reported by McCloskey et al. [33]. Nazar et al. found that homogeneously sized toroid-like products with 600–800 nm in diameter are comprised of nanocrystalline Li_2O_2 rods with dimensions of approximately 15 nm × 80 nm [34]. They also reported that the growth mechanism of Li_2O_2 is governed by the current density [24]. Small current densities cause aggregation of nucleated Li_2O_2 nanocrystallites; whereas large current densities lead to the quasi-amorphous thin films. Mitchell et al. found that at small discharge current densities, Li_2O_2 particles first form stacked thin plates, and then spontaneously splay. Consequently, secondary nucleation of new plates leads to the development of toroidal shapes. At large current densities, copious nucleation of equiaxed Li_2O_2 particles precedes growth of discs and toroids [35]. Zhai et al. reported morphologic evolution of the toroidal product during discharge, which increases in size and the shape evolves from ring torus to spherical-like toroids [36].

Previous studies showed that for a given design of the cathode (including pore shape and size as well as the electrode thickness), the morphology of the discharge product is affected by the electrochemical kinetics and associated transport of oxygen, lithium ions and electrons [24,35]. It would then be logical to expect that the operating temperature also affects the morphology of the discharge product, since it is intimately linked with the electrochemical kinetics and transport of the species [37,38]. To date, the relationship between the operating temperature and the morphology of the discharge product is not well understood. In this work, we experimentally studied the effect of the operating temperature on the morphology of the discharge product in non-aqueous lithium-air batteries. The batteries were discharged at various operating temperatures and current densities with a fixed capacity. The resulting product morphology was characterized and analyzed. Moreover, the relationship between the product morphology and the battery behavior at different operating temperatures was also investigated.

2. Experimental

2.1. Cathode fabrication

The cathode electrode was fabricated by casting a layer of carbon powder (Ketjen Black EC-600JD, specific surface area: 1334 m^2 g^{-1}) onto a carbon paper current collector (TGP-H-030, thickness: 100 μm) in three steps: i) mixing carbon powder with PTFE (as the binder) at a weight ratio of 9:1; ii) adding ethanol as a dispersing agent to form a slurry, which was ultrasonically stirred for 1 h; iii) casting the slurry onto the carbon paper uniformly. After being air-dried, the electrode was baked at 240 °C and sintered at 350 °C, for 1 h each, to make the binder (PTFE) distribute uniformly to connect the carbon power. Finally, the cathode electrode was cut into a disc with a diameter of 10 mm. The thickness of the cathode was about 105 μm, and the carbon powder loading was about 1.2 mg cm^{-2}.

2.2. Battery assembling and test

The lithium-air battery contains a lithium metal foil as the anode, a glass-fiber separator (Whatman GF/C), and the cathode as

prepared. 150 μL 1 M lithium Bis(Trifluoromethanesulfonyl)Imide (LiTFSI, Sigma–Aldrich, 99.95%) in tetraethylene glycol dimethyl ether (TEGDME, Sigma–Aldrich, 99%) was added into the battery to saturate the separator and the cathode. The solvent TEGDME was first soaked over a lithium metal foil for 10 h to remove moisture [27]. It was then distilled under vacuum and dissolved lithium salt (LiTFSI) to form the electrolyte and dried by molecular sieve. The battery was assembled in an argon-filled glove box (Etelux, Lab 2000) at water and oxygen contents below 1 ppm. The battery was then placed into a temperature-controlled chamber with a temperature fluctuation of ±0.1 °C. The inlet of the battery was tightly connected to high purity oxygen (≥99.997%, H_2O ≤ 1 ppm, CO_2 ≤ 1 ppm) with a constant flow to exhaust remaining argon. Then, the outlet of the battery was seal and the battery was exposed to oxygen at the constant pressure of about 1 atm. The discharge performance was examined galvanostatically (0.1, 0.2, and 0.3 mA cm^{-2}) using the battery cycling system (Neware, CT-3008W) at the controlled temperature of 21, 35 and 45 °C, respectively. To examine the effect of product morphology on the charge voltage and eliminate the influence of temperature, the cathodes discharged with a fixed capacity at different temperatures (21, 35 and 45 °C) were all charged at 21 °C at the current density of 0.3 mA cm^{-2}. The cycle performance at different temperatures was tested at the
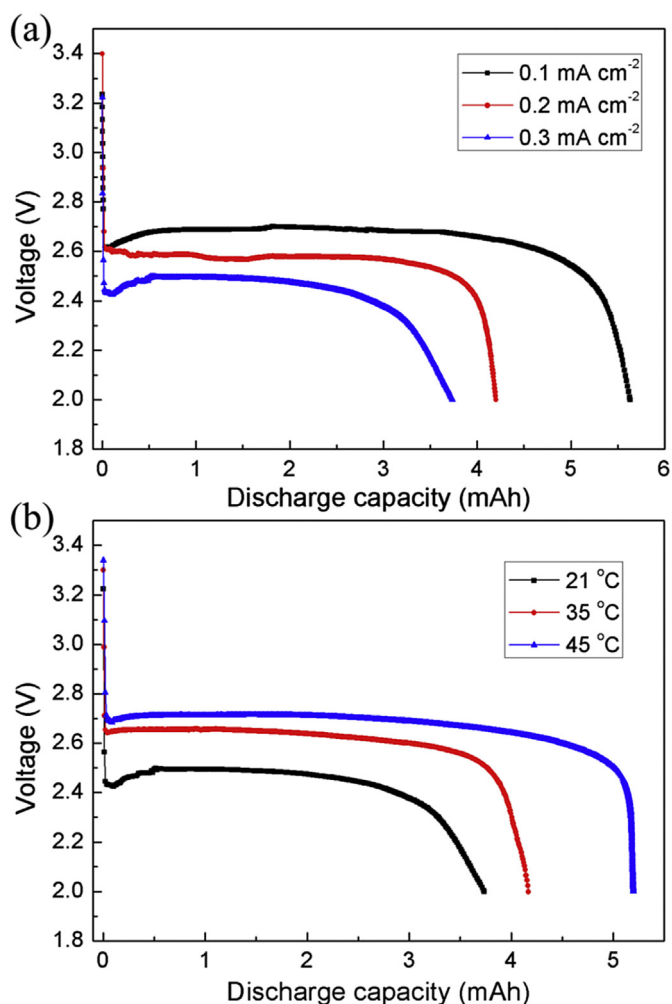

Fig. 1. Galvanostatic discharge curves with the cut-off voltage of 2.0 V: (a) at the operating temperature of 21 °C with the current density of 0.1, 0.2 and 0.3 mA cm^{-2}; (b) at the current density of 0.3 mA cm^{-2} with the operating temperature of 21, 35 and 45 °C.