



Screen printed cathode for non-aqueous lithium–oxygen batteries



C.Y. Jung, T.S. Zhao*, L. An, L. Zeng, Z.H. Wei

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

HIGHLIGHTS

- A screen-printed cathode is fabricated for non-aqueous Li–O₂ batteries.
- Screen-printing method creates sufficiently large pores for O₂ transport.
- Pores in the screen-printed cathode appropriately distribute the Li₂O₂ deposits.
- Battery's capacity and cyclability are improved with the screen-printed cathode.

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ABSTRACT

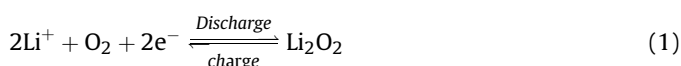
An issue with conventional non-aqueous Li–O₂ battery cathodes that are formed by spraying/brushing/casting/coating carbon black slurries is a lack of sufficiently large pores, vulnerable to clogging by solid discharge products, and hence resulting in a low capacity. In this work, we report a novel cathode structure formed by screen-printing method. This deposition method allows the creation of evenly distributed large pores (~10 μm). As compared with the cathode formed by slurry-coating method, the cathode formed by the present method increases the battery's capacity by two times. The cyclability is also seen a significant improvement. The improved performance may be attributed to large pores that give more appropriate distributions of discharge products and hence facilitate the transportation of oxygen during cycling.

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1. Introduction

Non-aqueous lithium (Li)–oxygen (O₂) batteries are exceedingly attractive technologies, with the potential to surpass the capability of current state-of-the-art Li-ion batteries, due to their high theoretical specific energy (11,680 Wh kg^{−1}) [1,2]. To unlock this battery's full potential, however, several technical issues must first be resolved. In particular, the reversibility with high capacity has yet to be established in order to develop a practical Li-air battery [3].

In the battery cycle, the following reaction is widely accepted [4–6]:



Main discharge product, lithium peroxide (Li₂O₂), is an electrical insulator and is deposited onto the cathode surfaces in the form of

solid product, due to its low solubility in aprotic solvents, e.g., tetraethylene glycol dimethyl ether (TEGDME) [7–9]. With an increase in the discharge depth, Li₂O₂ deposits gradually accumulate in the cathode and causes a serious capacity limitation through pore clogging and electrical passivation [10,11]. These obstacles may limit the transportation of O₂, Li ion and electron, leading to premature cell death [12]. Thus, it is imperative to investigate how different cathode structures with varying pore size and distribution affect the capacity.

Attempts to resolve this issue have involved the investigation of different carbon materials with varying porosities. Carbon is naturally porous material with high electrical conductivity [13–18]. By exploring several different types of conductive carbons, Kuboki et al. found that the larger pore volume significantly boosts the capacity regardless of the surface area [13]. Inspired by their work, Yang et al. investigated the pore size distribution of 4 different classes of carbon materials, namely, carbon black, carbon nanotube, graphite and mesoporous carbon, discovering that pore diameters larger than several tens of nanometers are beneficial in achieving higher capacity [14]. Similarly, Xiao et al. and other authors

* Corresponding author.

E-mail address: metzhao@ust.hk (T.S. Zhao).

reported that initial capacity relies heavily on the specific volume or surface area occupied by the meso-pores (2–50 nm) or macro-pores (>50 nm), while less dependent on micro-pores (<2 nm) [15–18].

Recently, several authors have evidenced abnormally large Li_2O_2 deposits (>1 μm), which are grown in disc or toroid shape [19–23]. These products consist of multiple number of Li_2O_2 crystallites in size of 7–25 nm, which are much larger in comparison to micro-pores [24–26]. Hence, the transportation of O_2 is found to be a limiting factor over electrical passivation within micro-porous cathode structure [26]. This is well supported in findings from Ding et al., who reported that pore diameter could be the most significant factor in determining the capacity, where the highest performance was achieved at an average pore size of 80–100 nm [27]. Because conventional carbon black electrode is mostly composed of micro-pores, a sufficient number of larger pores is absolutely necessary to facilitate the O_2 transport without severe clogging and hence improve the capacity [28]. Practically, the macro-pore fabrication is strongly dependent on deposition method [29–31]. However, the current literature lacks information on the fabrication of the $\text{Li}-\text{O}_2$ battery cathode structures through varying deposition methods.

In this work, we report a screen-printed cathode for non-aqueous $\text{Li}-\text{O}_2$ batteries. Sufficiently viscous carbon slurries are screen-printed through a dense silk mesh, by which the large crack-like pores are created and evenly distributed (Fig. 1). Subsequently, the cycle performance of the screen-printed cathode is examined in comparison to that of the slurry-coated cathode. With varying discharge depths, the morphology of the screen-printed cathode is visualized as an indicator of the pore volume utilization by Li_2O_2 . Furthermore, the capacity and cyclability of non-aqueous $\text{Li}-\text{O}_2$ batteries are discussed on different cathode structures created by slurry-coating and screen-printing methods.

2. Experimental

2.1. Cathode fabrication

For the polymer binder with ionic conductivity, 3 wt% lithiated Nafion dispersion is prepared by mixing 10 g of 5 wt% protonated Nafion dispersion (DE512, DuPont) and 6.8 ml of 0.1 M lithium hydroxide aqueous solution, followed by ultrasonication for 1 h. 3 wt% lithiated Nafion dispersion in 2-propanol (99 wt%, Sigma Aldrich) was obtained by solvent-exchange method. As shown in

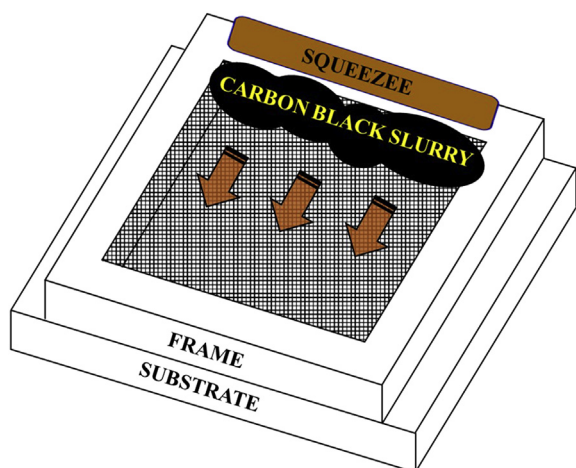


Fig. 1. An illustration of experimental setup of screen-printing deposition.

Fig. S1, the lithiated Nafion ionomer shifts the band assigned to $-\text{SO}_3^-$ symmetric stretch from 1056.1 to 1072.6 cm^{-1} due to the interaction between Li ion and oxygen, indicating that Li is substituted for hydrogen in the sulfonate group [32,33]. Subsequently, carbon black powder (EC-600 JD, Akzo Nobel) and lithiated Nafion dispersion are added into a solvent of 2-propanol to achieve a binder-to-carbon ratio of 1:4 (m/m). The carbon slurry is physically stirred until the desired viscosity is reached. As illustrated in Fig. 1, the prepared slurry is placed over the silk screen (200T, Wai Hang Co.), situated slightly above the substrate. Here, commercially available carbon paper (TGPH-060, Toray Industries Ltd.) is used as both substrate and current collector. The screen mesh was pressurized by a rubber Squeegee to coat the carbon black powder onto the carbon paper. For sake of uniformity, the distance between the screen mesh and the substrate is optimized to be 100 μm . Finally, the cathode samples are dried at 60 $^\circ\text{C}$ over 24 h prior to characterization. For comparison, the slurry-coated cathode is fabricated with an identical composition of the Nafion binder and carbon black powder.

2.2. Characterization

Attenuated total reflection (ATR) Fourier transform infrared spectroscopy (FTIR, Bruker, Vertex 70 Hyperion 1000) was performed for protonated and lithiated Nafion film prepared by solution-cast method. The morphology of the as-deposited cathode was investigated by scanning electron microscopy (SEM, JEOL Inc., JSM-6300) under an acceleration voltage of 20 kV. The pore size distribution was measured by mercury intrusion porosimetry (Micrometrics, Autopore IV 9500). After battery testing, the discharged cathodes were disassembled and cleansed with pure TEGDME (99 wt%, Sigma Aldrich) to examine their modified structures with varying discharge depths. X-ray diffraction (XRD, Panalytical, PW1825) analyses were also conducted by Cu K α radiation (0.154 nm), within 2θ value between 30 and 70 $^\circ$, to identify the composition of the solid discharge products.

2.3. Battery test

A single cell is designed to contain a Li foil, a glass microfiber separator (GF/C, Whatman) and a porous carbon cathode coated on the carbon paper, where 100 μL of 1 M lithium Bis(Tri-fluoromethanesulfonyl)imide (LiCF_3SO_3) (99.95 wt%, Sigma Aldrich) dissolved in TEGDME is used as an electrolyte. The water content in the electrolyte is less than 5 ppm, in order to avoid undesired side reactions, namely, formation of lithium hydroxide [34]. The battery was assembled with polytetrafluoro-ethylene fixture (T-810-6, Swagelok) in an argon-filled glove box (Lab 2000, Etelux) to minimize any contact with water molecules. At an ambient temperature, the cell was fed with high purity O_2 gas and stabilized for 2 h under open circuit condition. Subsequently, the cell was cycled at a specific current density of 200 mA g^{-1} , based on the mass of carbon powder (1 mg cm^{-2}), with discharge and charge cut-off voltages of 2.0 V and 4.5 V, respectively. Before each cycle, electrochemical impedance spectra (EIS) was measured at open circuit voltage with an impedance analyzer (Parostat 2273, Princeton Applied Research) in the frequency range of 300 kHz–0.01 Hz.

3. Results and discussion

3.1. Morphology of the as-deposited cathode

We recall that, for conventional carbon black cathodes, the capacity of non-aqueous $\text{Li}-\text{O}_2$ battery is strongly dependent on the

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