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Thermal restacking of graphene structure to improve lithium-air battery cyclability

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ABSTRACT

Poor rechargeability is one of major drawbacks of lithium-air batteries. Our study reveals that the accumulation and subsequent removal of reaction products during cycles can lead to a serious disruption and volume expansion of the cathode structure and demonstrates that by restacking and realigning the three phase interface of the cycled cathodes via mild heat treatment results in the enhanced cycle performance by over 200% and reduces the discharge overpotential at the same time. The results stress the importance of maintaining the physical configuration of lithium-air cathodes, and provide a new insight towards pulling out capacity retention of the system by better utilization of the available carbon surface.

1. Introduction

Lithium air or lithium oxygen (Li-O_2) batteries, one of the most promising candidates of energy storages for electric vehicles, have theoretical specific energy greater than lithium-ion batteries [1–3]. Li-O_2 batteries use oxidation of lithium at anode and reduction of oxygen at carbon cathode, creating the net electrochemical reaction, $2(Li^+ + e^-) + O_2 \leftrightarrow Li_2O_2$. ($U_0 = 2.96$ V versus Li/Li^+) [2–4]. Profound studies are being carried out with efforts to achieve efficient carbon surface utilization [5–7] and to overcome the major hurdle of cell degradation caused by parasitic reactions from carbon and electrolyte instability against superoxide nucleophilic attack [8–13]. Moreover, significant volume changes in both electrodes and consequential electrolyte leakage have also been discussed as the cause of capacity fading [14–16]. In this paper, we present the evidence of the occurrence of structural changes and propose a facile way of renewing the used cathodes by restoring the structure via mild heat treatment, namely thermal swing restacking (TSR). Notwithstanding the observed parasitic reactions due to carbon and electrolyte decomposition, the recovery of the interconnected network between carbon layers led to an improvement in the capacity retention by lowering the internal resistance of the cell.

2. Materials and methods

2.1. Cell fabrication

Lithium disc (MTI Corp.) was used as an anode. The electrolyte, 1 M $LiCF_3SO_3$ (Sigma-Aldrich) in 1,2-dimethoxyethane (DME), was prepared and impregnated into the glass fiber separator (Whatman). The cathode was made of reduced graphene oxide (RGO) (Dongjin Semichem) and Nafion (Ion Power) in isopropyl alcohol (Sigma-Aldrich) coated on a gas diffusion layer (Toray), in a weight ratio of 4:1. The amount of RGO loaded on the substrate was 0.1 ± 0.02 mg/cm^2. The cell was assembled in the argon filled glove box and purged with oxygen outside for 5 min.

2.2. Thermal restacking process

The cycled cathode was taken out from the cell and then heated at 120 °C for 1 h under argon atmosphere. After cooling down the heated cathode for another hour, the cell was re-opened and added with additional 110 μl of fresh electrolyte to the used glass fiber separator followed by placing the treated cathode.

2.3. Characterization

Electrochemical impedance spectroscopy (EIS) of the cell was evaluated using a PARSTAT 4000 (Princeton Applied Research) within a frequency range of 10^5 to 10^{-2} Hz using 5 mV (RMS) input. The morphology of RGO at each different state was observed by scanning electron microscope (SEM) (Tescan Mira3). The surface property was

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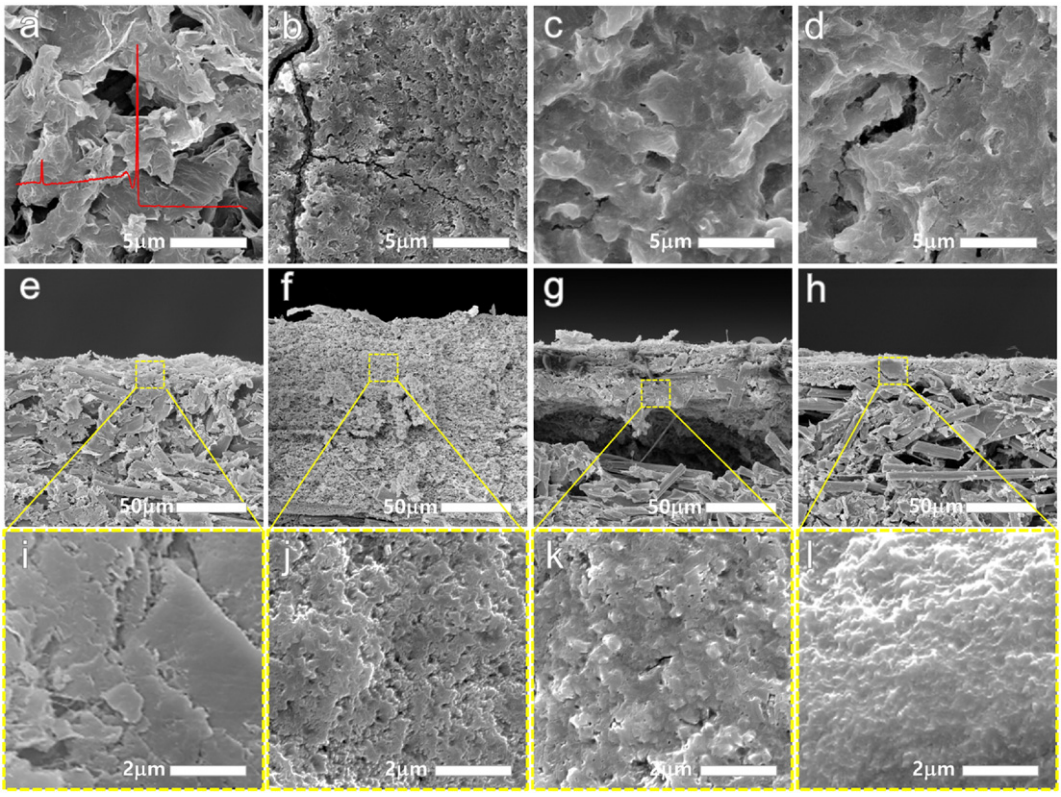

Fig. 1. SEM images of RGO coated air cathode at the (a,e,i) pristine, (b,f,j) discharged, (c,g,k) charged, and (d,h,l) thermally restacked states. (e–h) are cross-sectional images of the same electrodes as in (a–d), respectively. (i–l) are high resolution images of (e–h).

further investigated by X-ray photoelectron spectroscopy (XPS) (Surface Science Instruments) and Raman spectroscopy (Renishaw InVia). XPS operating pressure was ~2×10^{-9} Torr, and monochromatic Al K-alpha X-rays (1486.6 eV) were used with beam diameter of 1 mm. The Raman spectrum was collected from a nearly polarized 488 nm laser. N_2 isotherms were obtained from a Micromeritics Gemini VII 2390. The external pore size distribution was measured by capillary flow porometer (Porous Materials).

3. Results and discussion

The cross-sectional SEM images of RGO cathodes in Fig. 1e–h show significant structural changes during cycling. Comparing pristine cathode in Fig. 1e with the charged cathode in Fig. 1g, not only the thickness of RGO layer has increased but also sizable crevices were generated in the process of decomposing reaction products. Knowing that the glass transition temperature of Nafion resin, which was used as a binder for RGO cathode, is ~110 °C, heat treating the cathode at charged state at 120 °C successfully closed up the crevice as shown in Fig. 1h and reduced the overall thickness of RGO layer. Top view SEM images in Fig. 1a–d show that there is no sign of notable changes in the morphology of reaction products before and after the heat treatment.

XPS and Raman spectroscopy explicitly identified the reaction products formed on the air cathode during cell operation. (Fig. 2a–b) Both spectra results were commensurate in that two major compounds, Li_2O_2 and Li_2CO_3 were produced and were partially decomposed during

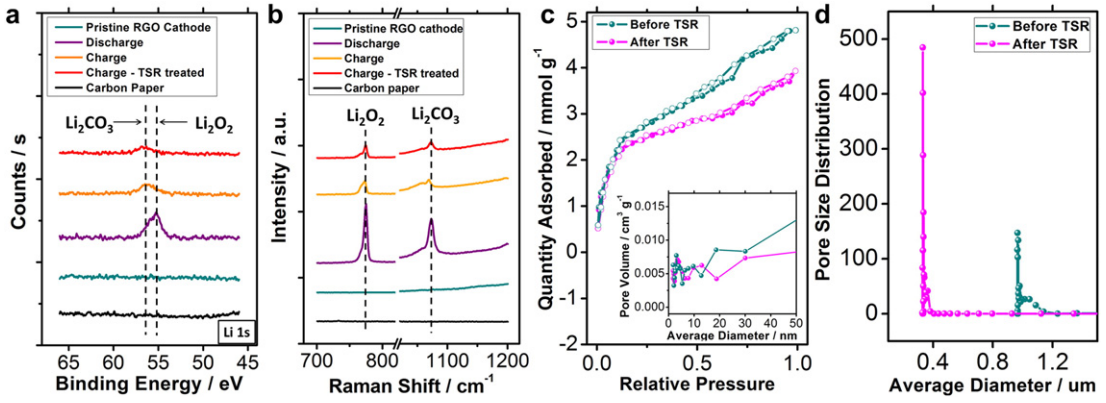

Fig. 2. Spectra results and pore size distribution. (a) Li 1 s XPS and (b) Raman spectrum of RGO coated substrate at the pristine, discharged, charged, and thermally restacked states. (c) N_2 isotherms and (d) capillary flow porometry data for RGO cathodes before and after the thermal treatment. The inset image in (c) provides the BJH pore size distributions calculated from the adsorption branch of the N_2 isotherms.