

Microstructural Characterization of Air Electrode Architectures in Lithium-Oxygen Batteries

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The aprotic Lithium-Oxygen (Li-O₂) batteries, consisting of lithium metal and porous air electrode separated by electrolyte, have the potential needed for long-range electric vehicles. The architectures of air electrodes are found to be of paramount importance to achieve good electronic and ionic conductivity, fast oxygen diffusion, and stable integrity for high-performance Li-O₂ batteries [1].

In this work, we first characterized an air electrode showing a dramatic reduction in charge overpotential [1]. We found that the nanostructured cathode architecture with an Al₂O₃ coating and Pd nanoparticles led to a nanocrystalline lithium peroxide (Li₂O₂) discharge product that contributes to the low overpotential. As shown in Fig. 1a, the pristine carbon (super P) surface has almost no amorphous phase. The carbon surface was partially coated with 3 cycles of Al₂O₃ (Fig. 1b) by atomic layer deposition to passivate carbon defect sites. The protective Al₂O₃ coating on the air cathode prevents electrolyte decomposition on carbon defect sites, which can increase the charge potential. Fig. 1c shows the Pd nanoparticles (2-6 nm) are often directly attached to the carbon support. The architecture of cathode promotes growth of a nanocrystalline form of discharged product Li₂O₂ as shown in Fig. 1d. Density functional theory calculations show that amorphous Li₂O₂ may have a metal-like density of states, in contrast to the poor electronic conductivity of crystalline Li₂O₂ [1]. The amorphous Li₂O₂ in the grain boundaries improves electronic transport properties that are needed to lower the charge potential. Fig. 1e shows a dramatic reduction in overpotential of ~0.2V during charge using the nanostructured cathode architecture.

To further understand the effect of metal nanoparticle on the growth of Li₂O₂, subnanometer silver clusters of defined size and number of atoms were deposited on passivated carbon [2]. Fig. 2a shows a TEM image of a 15 atom Ag cluster (Ag₁₅) on an Al₂O₃ coated carbon particle. In most cases, discrete Ag₁₅ clusters are observed. Occasionally, agglomeration of the Ag₁₅ clusters (circled in Fig. 2a) is observed. Fig. 2b shows the atomic structure in an Ag₁₅ cluster from a video (1 frame per second). The atomic arrangement of the clusters changes quickly under the electron beam, so very low-dose imaging techniques were required to obtain these images. SEM observation indicates that dramatically different morphologies of the discharged product Li₂O₂ is dependent on the size of the Ag clusters [3]. The Li₂O₂ product using Ag₃ clusters as a catalyst is film-like. In contrast, the discharge product using Ag₉ clusters is largely toroid-like with rough surfaces, while Li₂O₂ toroids obtained using the Ag₁₅-based cathode have smooth surfaces. The discharge capacity (~3500 mAhg⁻¹) for the first cycle of the cell with the Ag₁₅-based cathode is much larger than that using the Ag₃ and Ag₉ clusters (~2400 mAhg⁻¹). The results of this study indicate that precise control of subnanometer size of catalytic nanoparticles on air electrodes can be used as a means to improve the performance of lithium-oxygen cells [3,4].

References:

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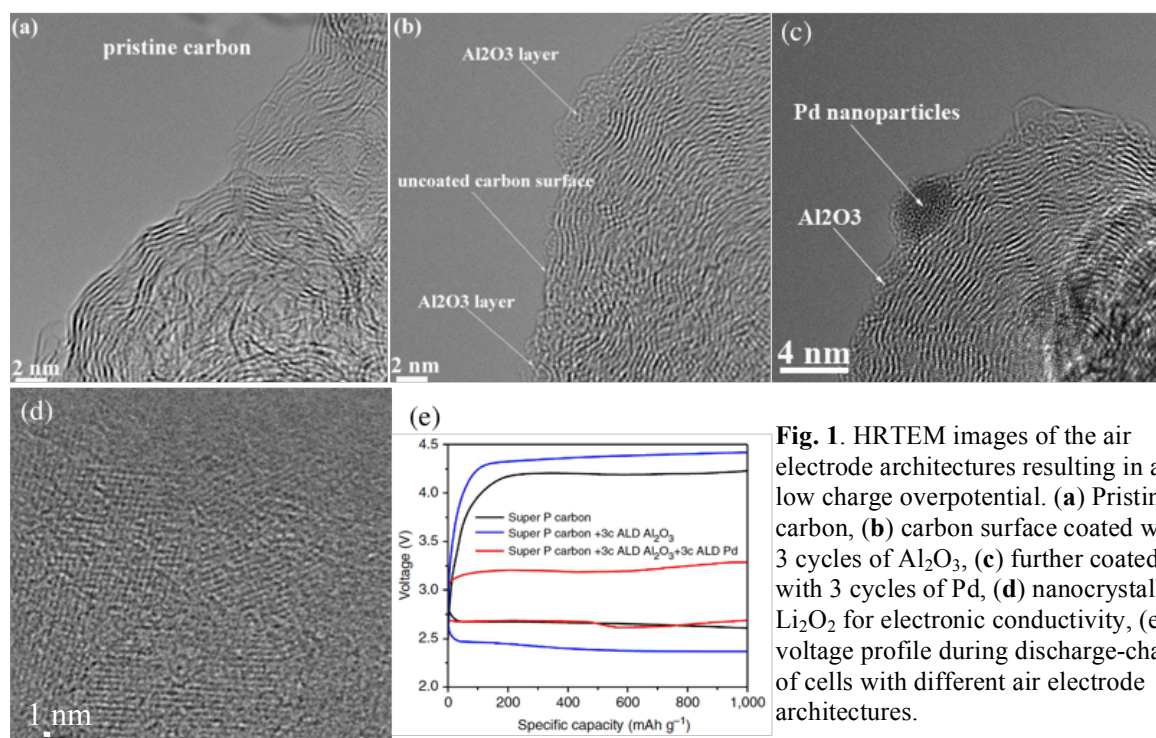


Fig. 1. HRTEM images of the air electrode architectures resulting in a low charge overpotential. (a) Pristine carbon, (b) carbon surface coated with 3 cycles of Al_2O_3 , (c) further coated with 3 cycles of Pd, (d) nanocrystalline Li_2O_2 for electronic conductivity, (e) voltage profile during discharge-charge of cells with different air electrode architectures.

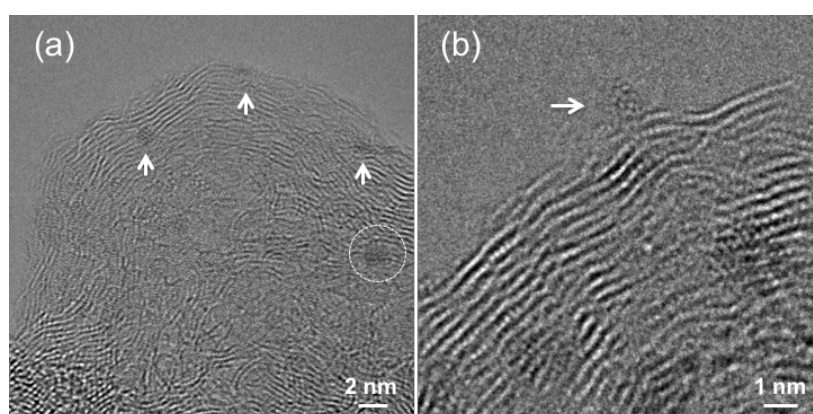


Fig. 2. HRTEM images of the air electrode architectures leading to the control of Li_2O_2 morphologies. (a) TEM image of Ag15 clusters (arrows) on an Al_2O_3 coated carbon particle. Occasionally, agglomeration of Ag15 clusters (circled) is observed. (b) HRTEM image of an Ag15 cluster on an Al_2O_3 coated carbon surface.