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A simple method for surface modification of carbon by polydopamine coating for enhanced Li–air batteries

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ABSTRACT

We demonstrate a simple method for enhancing the electrochemical performance of air electrodes of Li–air batteries using a polydopamine coating on the surface of carbon. A thin polydopamine layer on Ketjen black carbon clearly modified the surface properties of the air electrode, in turn resulting in improved electrolyte filling. The coating also passivates surface carbon defects, which may be helpful in suppressing parasitic reactions during cycling. Electrochemical tests of the electrode indicate that the introduction of the polydopamine layer is beneficial in that it increases the capacity, lowers the overpotential, and improves the cyclic performance of Li–air cells. These effects may be associated with the increased active catalytic area of the electrode, mostly resulting from the improved wetting characteristics. The suppression of parasitic reactions due to the passivation of carbon defects also contributes to the enhanced cyclic performance of the polydopamine-treated electrode.

1. Introduction

Recently, lithium–air batteries have received worldwide attention because they can provide capacities that are several times higher than those of commercial Li-ion batteries [1–6]. In a Li–air cell, the air electrode, composed of carbon and a catalyst, plays a key role in determining the discharge capacity and cyclic performance of the cell [7–13]. Oxygen, the active material in the cathode of a Li–air cell, reacts with the lithium ions supplied by the anode at the surface of the air electrode. If a non-aqueous electrolyte is used, the oxygen must dissolve in the electrolyte at the cathode/oxygen interface before the reaction with lithium ions can proceed [14,15]. Accordingly, the filling of the air electrode by the electrolyte is an important part of the reaction kinetics of the cell.

Scheme 1 schematically illustrates the relationship between electrolyte filling and catalytic reactions in an air electrode [15]. In the most frequently encountered case (Scheme 1(a)), a part of the air electrode is flooded by electrolyte, and the other part is exposed to air. Because the solubility of oxygen in the organic electrolyte is low, the reaction between oxygen and lithium ions in a deeply flooded electrode may be inefficient. In this case, most of the reaction will occur at the interface between the gaseous oxygen and the air electrode. An air electrode that is coated by a thin electrolyte layer is ideal with respect to the reaction kinetics, as shown schematically in Scheme 1(b). In this case, it is possible to maintain the short diffusion length and uniform concentration of oxygen throughout the electrode area [14,15], which implies that the optimal area of the air electrode can be used during the reaction.

This work was motivated by the notion that if the wettability of the carbon by the electrolyte is enhanced, the surface area of the electrode that can effectively participate in the reaction between oxygen and lithium ions can be increased. To modify the surface of carbon, an additional material component of the air electrode was introduced, namely a polydopamine coating. Polydopamine was discovered during an analysis of the adhesion ability of mussels [16–22], and polydopamine coatings are very effective in modifying the surface properties of various organic and inorganic surfaces [23]. In particular, polydopamine-treated surfaces have shown enhanced wettability with organic electrolytes which are already widely used in Li batteries [24]. Moreover, the polydopamine coating is also expected to assist the retention of the electrolyte at the non-submerged regions of the electrode [23]. Commercial Ketjen black was used as the carbon material because it is inexpensive, has high electrical conductivity, and has a large specific surface area.

In our study, no oxide catalyst was used for the air electrode in order to characterize the influence of the surface-modified carbon on the electrochemical performance of the cell. The carbon component not only provides reaction sites but also acts as catalyst. An electrode employing polydopamine-coated Ketjen black

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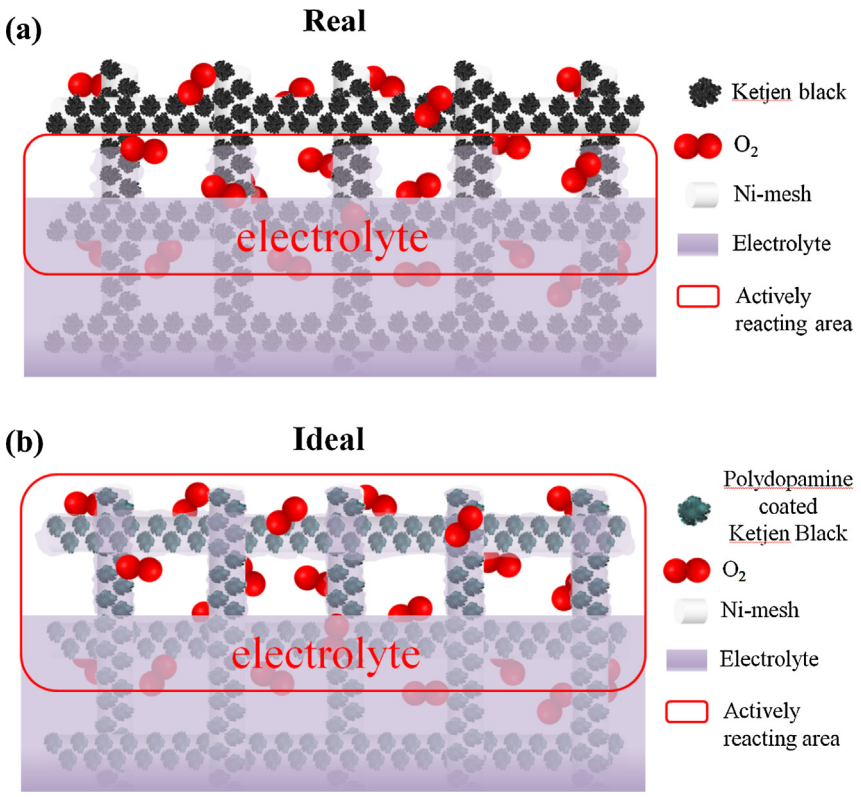

Scheme 1. *Scheme of electrolyte filling.* (a) Real and (b) ideal electrolyte filling of the electrode [15].

is expected to have enhanced electrochemical properties because the polydopamine coating improves the wettability with the electrolyte.

2. Experimental

Commercial-grade Ketjen black was immersed in a solution of dopamine in 10 mM tris-buffer/methanol (1:1 v/v, pH 8.5) for 5 min at room temperature. This forms a polydopamine layer on top of the surface of the carbon particles via self-polymerization. This suspension was centrifuged, and the resulting solid was washed with distilled water and then with an ethanol solution, following which it was dried. The microstructure of the Ketjen black/polydopamine electrodes was observed using transmission electron microscopy (TEM) on a JEOL-JEM 2100F microscope (JEOL, Japan). X-ray photoelectron spectroscopy (XPS) on a VG Microtech ESCA2000 was used to investigate the nature of the pristine and polydopamine-coated surface of Ketjen black.

The electrochemical performance of the Ketjen black electrode was examined using a modified Swagelok cell consisting of an air electrode, a metallic Li anode, a glass-filter separator (Whatman), and an electrolyte consisting of 1 M LiTFSi in tetraethylene glycol dimethyl ether (TEGDME). The air electrode contained 90 wt% of Ketjen black and 10 wt% of poly(vinylidene fluoride) (PVDF) binder. All components were ball-milled to ensure homogeneous mixing, following which they were coated on a Ni mesh. The loading weight of the electrodes was adjusted to $1.0 \pm 0.1\ mg\ cm^{-2}$. The cells were assembled in an Ar-filled glove box and subjected to galvanostatic cycling using a charge-discharge system in the voltage range of 2.35–4.35 V. The experiments were carried out under O_2 (1 atm) in a sealed chamber. The morphology of the cycled electrodes was observed using high-resolution scanning electron microscopy (SEM) on a Nova Nano 200. Fourier-transform infrared spectroscopy (FTIR) of the electrodes was performed on a FT-IR-4200 (JASCO) instrument to check the reaction products accumulated during cycling.

3. Results and Discussion

It should be noted that the polydopamine coating on the surface of carbon is non-conducting and a hindrance to the movement of electrons. Therefore, the polydopamine layer should be as thin as possible to minimize this negative effect. In this work, Ketjen black was immersed in dopamine solution for just 5 min. Because the thickness of the polydopamine layer depends on the self-polymerization time [17,18], a thin polydopamine layer is expected to be formed on the surface of Ketjen black.

Fig. 1 shows TEM images of pristine and polydopamine-coated Ketjen black particles. The shapes of these pristine Ketjen black particles were nonuniform, but all had smooth outer surfaces (Fig. 1(a) and 1(c)). Unlike the pristine sample, the surface of the polydopamine-treated Ketjen black seemed to be covered by a thin film, as shown in Fig. 1(d), which may represent the polydopamine layer. However, it was difficult to clearly distinguish between the bare Ketjen black and the layer because Ketjen black has an amorphous structure and the layer is extremely thin. The small rectangles in Fig. 1(e) and 1(f) are used for the compositional analysis of the surface of Ketjen black by energy-dispersive spectroscopy (EDS). The surface of the polydopamine-coated Ketjen black contained a significantly higher content of N (~9.3 wt%) than the surface of pristine one, thereby demonstrating the existence of the polydopamine layer. Fig. 1(g)-(i) present the TEM-EDS maps for C and N. The intensity of the pixels shows the concentration of the elements. Not only C but also N is all uniformly distributed over the analyzed particle-area, indicating that the particles are homogeneously covered with polydopamine layer. The formation of the polydopamine layer could also be confirmed by XPS analysis. Fig. 2 shows the XPS spectra of pristine and polydopamine-coated