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Nickel-Foam-Supported Reticular CoO–Li_2O Composite Anode Materials for Lithium Ion Batteries**

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Since the early 1990s[1] people everywhere have been enjoying the great convenience brought about in daily life through the use of rechargeable lithium-ion batteries (LIBs): Modern portable consumer electronics such as laptops, cellular phones, camcorders, and MP3 players are mostly powered by LIBs. Compared with other battery systems, LIBs show the advantages of high energy density, long cycle and shelf life, and no memory effect. The search for better electrode materials has been the most dynamic motivation behind the research and development of lithium-ion batteries.[2–10] Graphite is the state-of-the-art anode material with a specific capacity of 320–340 $mA\,h\,g^{-1}$ (theoretically 372 $mA\,h\,g^{-1}$).[11,12] Transition metal oxides such as CoO and Cu_2O represent a new class of anode material with significantly higher capacities up to 800 $mA\,h\,g^{-1}$.[5,7,13–15] However, such a high capacity can only be achieved with the help of

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carbon additives, and is accompanied by a large irreversible capacity loss of up to 30%. Graphite-based composite electrodes that are modified with metal oxides (for example, SnO, CuO, and NiO) have displayed increased first-cycle lithiation capacity, but with even greater capacity loss.[16–18]

Here we present a new carbon-free anode, that is, CoO–Li_2O composite films, prepared by the electrostatic spray deposition (ESD) technique.[19–21] The structure of the films is controlled as a novel reticular morphology supported on a conducting nickel-foam substrate. This new composite electrode has an initial capacity loss of only 16.4% and 13% at 0.2C and 1C cycling rates, respectively, and yet retains a very high capacity (up to 877 $mA\,h\,g^{-1}$ at a 0.2C rate) and excellent rate capability.

The first novelty of our study is the use of a very porous nickel-foam substrate (Figure 1a) rather than a conventional dense metal foil (for example, copper) as the current collector. This change results in maximization of the contact area between the electrode and the electrolyte. Similar to the well-established results obtained with a dense substrate,[19] depending on whether nitrates or acetates are used as the precursors, dense (Figure 1b) or reticular films (Figure 1c) are formed. The thickness of the reticular film is about 30 μm (Figure 1d). The formation of film textures that show a very high degree of conformity to the substrates represents an advantage of the ESD technique. It results from a preferential landing mechanism in ESD, that is, the charged droplets of a precursor solution may "land" preferentially on the conducting parts of a substrate and become discharged there.

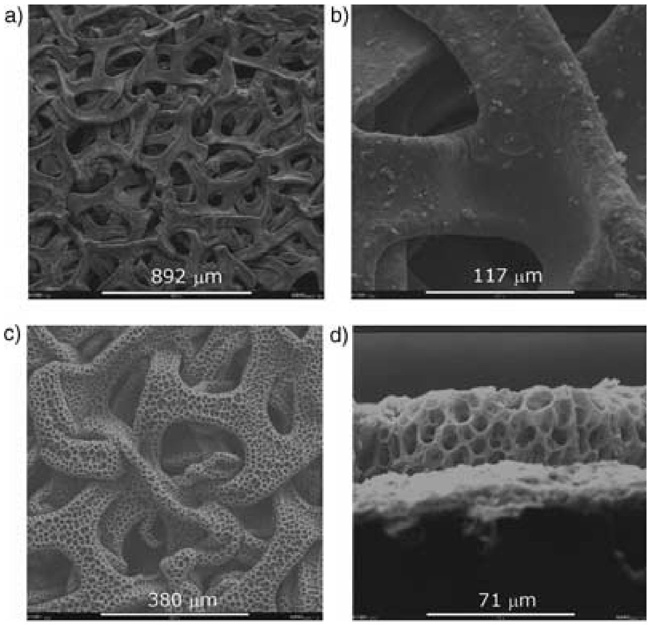

Figure 1. SEM images of the substrate and the CoO–Li_2O thin films. a) The porous nickel-foam substrate; b) surface morphology of a dense film from nitrate precursors; c) surface morphology of a reticular film from acetate precursors; d) cross-section of the reticular film from c). See the Experimental Section.

Except for the diffraction peaks from the nickel substrate, no other peaks can be discerned from the X-ray diffraction patterns (not shown). However, the X-ray diffraction patterns of the as-deposited films prepared under the same conditions but on an aluminum-foil substrate (lighter than nickel) clearly show the diffraction peaks from CoO in addition to those from the aluminum substrate (Figure 2). Nevertheless, the weak and broad CoO peaks indicate that the CoO in the films must be nanocrystalline or even amorphous. No peak is seen for any lithium compound, suggesting that the lithium product, which can be reasonably believed to be Li_2O formed at 235 °C, is amorphous. Therefore, the film is a CoO–Li_2O composite. The introduction of Li_2O, which alone is usually thought as an inactive component, in the composite is the second novelty of this work.

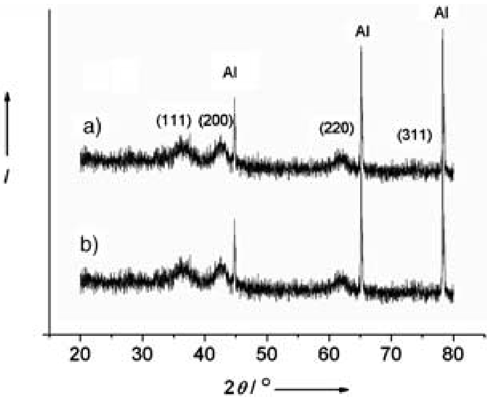

Figure 2. The X-ray diffraction patterns of the CoO–Li_2O thin films deposited on the aluminum substrate at 235 °C in air. a) Dense film; b) reticular film. The diffraction peaks from CoO are indexed in the patterns. I = intensity.

The voltage profiles of the electrochemical cells CoO–Li_2O/Li (Figure 3a,b) indicate that these composite electrodes have the typical characteristics of CoO electrodes, that is, a long voltage plateau at about 0.75 V followed by a sloping discharge curve down to the cut-off voltage of 0.01 V during the first discharge step.[5] After the first discharge, the 0.75 V discharge plateau does not appear anymore, suggesting a heterogeneous reaction mechanism of lithium insertion and extraction.[10,14,22] Remarkably, the first discharge step delivers a specific capacity of 900 $mA\,h\,g^{-1}$ for the reticular CoO–Li_2O film (1:1 Co/Li molar ratio; Figure 3a) and 730 $mA\,h\,g^{-1}$ for the dense CoO–Li_2O film (Co/Li 1:1; Figure 3b) at a current density of 0.1 $mA\,cm^{-2}$. Both values are significantly higher than the theoretical capacity (596 $mA\,h\,g^{-1}$) expected if only the film component CoO is active. On the other hand, the surface of the nickel substrate can be slightly oxidized at 235 °C in air. An independent measurement on an oxidized nickel substrate showed that the capacity owing to the substrate could account for about 10% of the total capacity of the reticular electrode film (see the Supporting Information). Even if the contribution from the substrate is discounted, the capacity of the electrode is still markedly higher than 596 $mA\,h\,g^{-1}$. Tarascon et al. have established that the extra capacity is likely due to the reversible formation and decomposition of a polymeric gel-like film on the surface of the CoO particles.[14,15] This film results from kinetically activated electrolyte degradation enabled by the active metal nanoparticles (Co). The presence of the film component Li_2O

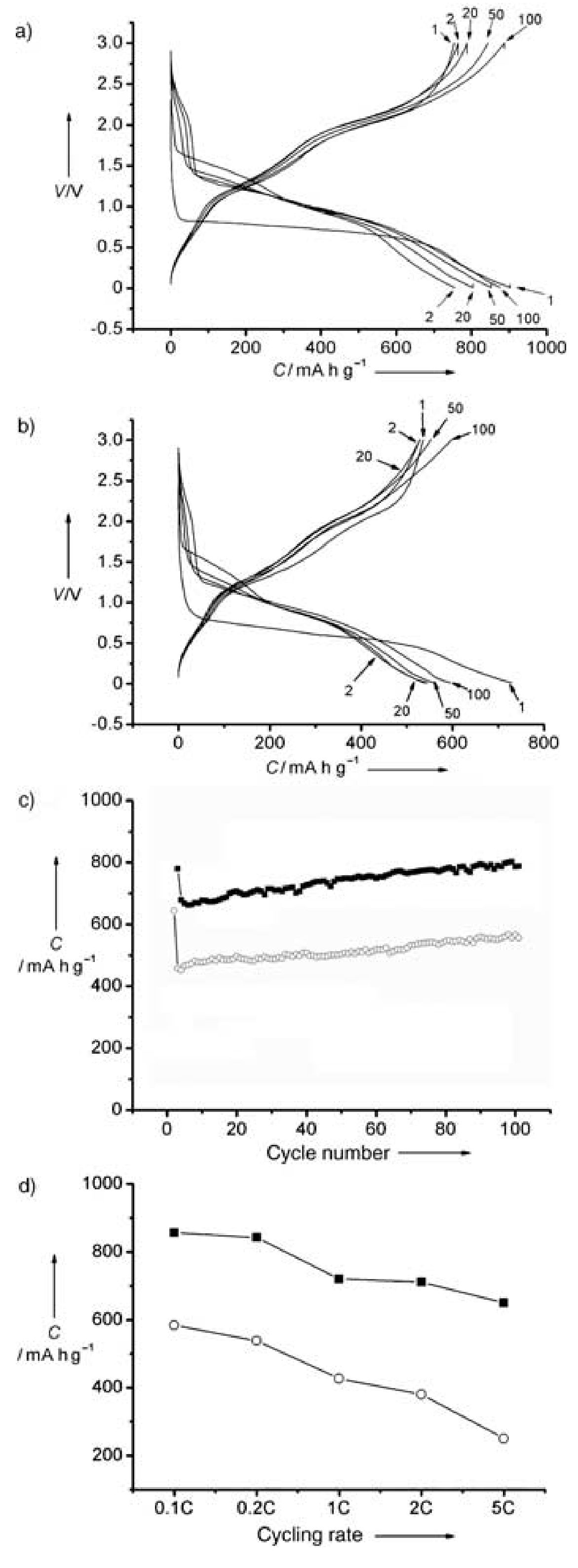

Figure 3. The electrochemical performance of the CoO–Li_2O thin-film electrodes cycled between 0.01 V and 3 V vs. Li^+/Li. a), b) Plots of the voltage–capacity curves of a reticular (a) and a dense (b) CoO–Li_2O film at a cycling rate of 0.2C (the numbers indicate the cycle number); c) the capacity–cycle-number curves of the CoO–Li_2O films at a cycling rate of 1C; d) the discharge capacity of the CoO–Li_2O films as a function of the cycling rate (0.1C–5C). ■ = reticular film, ○ = dense film; C = capacity, V = cell voltage.

may prohibit the growth of CoO particles and thus create a maximum CoO surface area. Hence, the capacity associated with the polymeric film is maximized.

The discharge capacity of the CoO–Li_2O composite films at a 0.2C cycling rate drops from 903 to 755 mA h g^{-1} for the reticular morphology (Figure 3 a) and from 729 to 538 mA h g^{-1} for the dense morphology (Figure 3 b) after the first cycle. However, the discharge capacity is gradually restored during the subsequent cycles; at the 100th cycle, it is 877 and 595 mA h g^{-1} for the reticular and dense films, respectively. At a higher current density of about 1C rate, the capacity of the CoO–Li_2O composite films follows a similar trend as for a lower current density, although the values at different cycles decrease a little (Figure 3 c). For the reticular CoO–Li_2O film, the specific capacity is 781 (1st cycle), 679 (2nd), 673 (10th), 695 (20th), 779 (80th), and 788 mA h g^{-1} (100th). The phenomenon of an initial drop in capacity followed by a gradual increase (Figure 3 c) is well documented in the literature, and is attributed to some irreversible Li_2O generated in the first discharge step.[14,23] Nonetheless, in the present study, the rise in capacity during cycling is also partly attributed to the increase in Co valence (see below). The reticular film also shows excellent rate capability; it reaches a specific capacity of 650 mA h g^{-1} when cycled at a 5C rate (Figure 3 d). For comparison, the 5C rate capacity is only 250 mA h g^{-1} for the dense film. The difference in the rate capabilities for the two different morphologies originates from the difference in their impedance (see the Supporting Information); the reticular film leads to relatively small cell impedance. The high capacity achieved at a high cycling rate implies that this electrode can be used for high-power applications such as hybrid electric vehicles (HEV).

To investigate the effect of composite composition (that is, the Li/Co molar ratio) on the electrochemical performance, we prepared reticular films of five different Li/Co ratios ranging from 1:4 to 4:1. We found that there is an optimal composition around Li/Co = 1 for achieving a maximum specific capacity. The capacity of the cells measured at a 1C rate is shown in Figure 4. The capacity of the cells with the two extreme compositions is 545 mA h g^{-1} for Li/Co = 1:4 and 267 mA h g^{-1} for Li/Co = 4:1. According to the curve shape, it is expected that pure CoO must have a reasonably high capacity while pure Li_2O is electrochemically inactive. In fact, it is difficult to prepare a reticular-structured pure CoO film under similar deposition conditions. The electrochemical performance of the non-reticular CoO film is markedly worse than that of the Li_2O-containing composite films (see the Supporting Information).

As mentioned before, the Li_2O in the composite plays an important role in optimizing and even enhancing the electrochemical performance of the CoO component. Firstly, as Li_2O prohibits the particle growth of CoO, a maximized CoO surface area may be obtained so that the capacity related to the polymeric gel-like film can be enhanced. Secondly, Li_2O is an oxidant that converts CoO into Co_3O_4 or even Co_2O_3 during cycling according to the reactions (1) or (2), where the

$$Li_2O + 3\,CoO \rightarrow Co_3O_4 + 2\,Li \tag{1}$$

$$Li_2O + 2\,CoO \rightarrow Co_2O_3 + 2\,Li \tag{2}$$

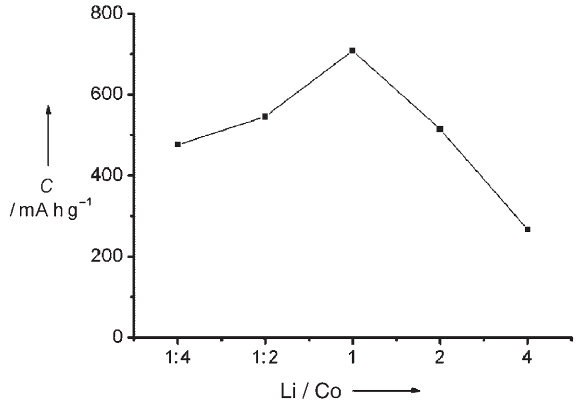

Figure 4. Plot of the discharge capacity of reticular CoO–Li_2O thin-film electrodes as a function of the Li/Co molar ratio in the precursor solutions. The cycling rate was 1C.

Li from Li_2O is transferred to the lithium metal electrode. The resulting increase in valency of the Co ions must partly account for the capacity that exceeds the theoretical value and the capacity rise of the composite films (Figure 3). The Li/Co molar ratios derived from these two reactions are 2:3 and 1:1, respectively, which are close to the optimal Li/Co ratio (Figure 4).

With a reticular CoO–Li_2O film (Li/Co 1:1) on a copper foil substrate, we confirmed the conversion of CoO into Co_3O_4 after five cycles (Figure 5). The third role of Li_2O is its likely buffering effect by relieving the stress caused by the volume change during the reduction of CoO, so that the structural integrity of the electrode can be readily maintained. Notable is the absence of a carbon additive in the composite films studied in this work. The nickel-foam substrate provides an excellent electronic conduction pathway for the electrochemical processes.

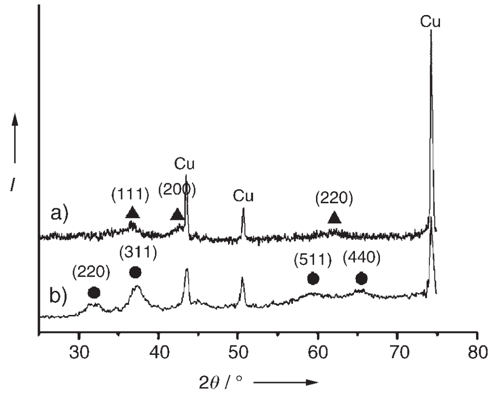

Figure 5. The X-ray diffraction patterns of CoO–Li_2O thin films (Li/Co 1:1) on a Cu foil substrate: as-deposited (a) and disassembled from a fully charged cell after five cycles (b). The diffraction peaks of CoO and Co_3O_4 are indexed in the patterns. ▲ = CoO, ● = Co_3O_4; I = intensity.

In conclusion, carbon-free CoO–Li_2O composite films with a novel reticular morphology supported on a conducting nickel-foam substrate have been prepared by the ESD technique. The initial discharge capacity of a CoO–Li_2O film (Li/Co 1:1) reaches 903 mA h g^{-1} with a first-cycle capacity loss of only 16.4 %. After 100 cycles, this film electrode retains a discharge capacity of 877 mA h g^{-1}. It also shows excellent rate capability with a 5C-rate capacity of up to 650 mA h g^{-1}. The Li_2O component in the composite is believed to play a threefold role: as a prohibitor for the CoO particle growth during synthesis, as an oxidizer for the conversion of Co^{2+} to Co^{3+}, and as a structural buffer. Such a composite anode opens the possibility of producing lithium-ion batteries with higher energy densities.

Experimental Section

With a precursor solution of lithium and cobalt acetates or nitrates in butyl carbitol ($CH_3(CH_2)_3OCH_2OCH_2CH_2OH$; 0.005 M), composite films of cobalt oxide and lithium oxide were deposited by the ESD technique for 2 h on a nickel-foam substrate heated at 235 °C (feeding rate 4 mL h^{-1}). A distance of 2–3 cm was kept between the needle and the substrate; the applied voltage was 11–13 kV. The composition and crystal structures of the as-deposited films were characterized by X-ray diffraction. The surface morphology was analyzed with a scanning electron microscope (Hitachi X-650).

The CoO-Li_2O films were used as the electrodes of electrochemical cells CoO–Li_2O/Li with 1 M $LiPF_6$ in ethylene carbonate and diethyl carbonate (EC/DEC 1:1 v/v) as the electrolyte. The cells were assembled in an argon-filled glove box (MBRAUN LABMASTER 130; moisture and oxygen levels less than 1 ppm) and cycled in the voltage range between 3.0 V and 0.01 V with a battery test system (NEWARE BTS-610).

To study the phase evolution of the CoO–Li_2O electrodes during cell cycling, a reticular CoO–Li_2O film (Li/Co 1:1) on a was deposited copper-foil substrate and assembled into a CoO–Li_2O/Li cell. The as-deposited film and the film disassembled from a fully charged cell after five cycles were characterized by X-ray diffraction.

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