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Effect of Lithia and Substrate on the Electrochemical Performance of a Lithia/Cobalt Oxide Composite Thin-Film Anode

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Abstract: Highly porous reticular Li_2O/CoO composite thin films fabricated by electrostatic spray deposition were investigated by using X-ray diffraction, scanning electron microscopy, galvanostatic cell-cycling measurements, and AC impedance spectroscopy measurements. The results of the electrochemical tests indicate that the initial coulombic efficiency and capacity retention are dependent on Li_2O content and the specific surface area of the deposited layer. Irrespective of the type of substrate, the electrode gave the best electrochemical performance when the molar ratio of Li to Co was controlled at 1:1. At the optimal composition, at 0.2 C the initial coulombic efficiency was as high as 81.9 % and 83.6 % for the film on Cu foil and on porous Ni, respectively. The Li_2O/CoO (Li/Co = 1:1) films on Ni foam and Cu foil had sustained capacities of up to 790 and 715 mAh g^{-1}, respectively, at a rate of 1 C over 100 cycles at 25 °C. Similar cycling experiments carried out at 70 °C showed that the capacity is temperature-sensitive, and it exhibited reversible capacities as high as 1018 (Cu foil) and 1269 mAh g^{-1} (Ni foam) for up to 100 cycles. The thin-film electrodes on Ni foam always performed better than those on Cu foil. Cycling at elevated temperature (70 °C) also resulted in a significant increase in capacity.

Keywords: cobalt · electrochemistry · electrostatic spray deposition · lithium · thin films

Introduction

Thanks to the efforts of Tarascon and co-workers, nanosized transition-metal oxides have been widely studied in recent years in search of new anode materials for Li ion batteries.[1,2] This group investigated a variety of transition-metal oxides M_xO_y, such as NiO,[1] Fe_2O_3,[3,4] CoO,[5] CuO,[6–8] Cu_2O,[9] and Co_3O_4,[10,11] as anode materials and proposed a new mechanism of lithium interaction that is different from the classical Li insertion/deinsertion or Li-alloying process. This mechanism involves the reversible formation and decomposition of Li_2O, accompanied by the reduction and oxidation of metal oxides. Among them, cobalt oxides (CoO_x) demonstrate the best electrochemical properties as lithium storage materials in Li ion cells. Nevertheless, because their initial coulombic efficiency (usually below 70 %) is too low for them to be utilized as practical anode materials for Li ion batteries, they have not yet been commercialized. It is commonly recognized that the formation of the solid–electrolyte interface (SEI) and the incomplete decomposition of Li_2O during the first charge process may be the main reason for the low initial coulombic efficiency.[12,13]

In our study of thin-film electrodes prepared by electrostatic spray deposition (ESD),[14–17] we recently found that the coulombic efficiency can be increased to 87 % by introducing Li_2O to CoO to form a carbon-free composite-oxide anode.[18] Li_2O plays a threefold role: as a prohibitor of CoO particle growth during synthesis, as an oxidizer for the conversion of Co^{2+} into Co^{3+}, and as a structural buffer. Furthermore, the film texture is very important: a highly porous reticular film is better than a dense film. The substrate used in that study was highly porous nickel foam. On the other hand, such a reticular texture can also be obtained on a dense substrate by ESD.[15–17] Dense copper foil is in fact the most widely used current collector of negative electrodes in commercialized lithium ion batteries. Herein, therefore, we investigate the effect of the substrate as well as its electrochemical behavior on electrochemical performance at an elevated temperature. We found that thin films on dense copper substrate also showed rather good electrochemical performance, especially at 70 °C.

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Results and discussion

Structural Analyses of CoO/Li_2O Thin Films

The XRD patterns of the deposited films on Cu foil or nickel foam are the same as those reported in reference [18], which can be indexed by the diffraction of CoO and Li_2O. Thus, under the specific ESD conditions, that is, under ambient atmosphere and at 235 °C, the cobalt component formed in the film was present in the form of CoO. Notably, only Co_3O_4 powder instead of CoO was obtained when cobalt acetate was decomposed in air at 235 °C. The difference in the decomposition product is probably due to the presence of butyl carbitol solvent in the case of ESD. In fact, when cobalt acetate was dissolved in butyl carbitol, the precursor solution turned dark green (instead of pink for Co^{2+} ions). This color change may imply a certain complexation reaction between Co^{2+} and butyl carbitol, and, accordingly, the low valence state (+2) was easily preserved in the deposited films. Of course, further investigation is needed to confirm this postulation.

Figure 1 a and b shows the scanning electron micrographs of two deposited films on Ni foam and Cu foil, respectively. Both of them are reticular structures with 3D cross-linked pores with a mean pore size of 10–15 μm. Clearly, the film on the Ni foam is more porous and has a higher specific surface area than that on copper foil. The SEM image at a higher magnification (Figure 1 c) shows that the reticular structure is composed of nearly monodispersed spheres with an average size of about 400 nm. This reticular morphology is characteristic of ESD films.[15–20] Smyrl and co-workers demonstrated that materials with a porous structure are excellent candidates for the design of high-performance batteries.[21,22] Hence, these reticular films are very advantageous as electrode materials owing to their very high specific surface area and good mechanical strength. Herein, all the films of different Li/Co ratios on different substrates were made with this reticular morphology.

Abstract in Chinese:

本文利用静电喷雾沉积（ESD）技术在铜箔和泡沫镍两种衬底上制备了网状多孔结构的 Li_2O/CoO 复合氧化物薄膜，并对其结构和性能进行了 X– 射线衍射（XRD）、扫描电镜（SEM），电池循环和交流阻抗谱测试。结果表明，薄膜电极的初始库仑效率及容量保持率明显取决于薄膜的 Li_2O 含量和比表面积。当 Li/Co 摩尔比为 1:1 时，无论何种衬底，薄膜电极的电化学性能最佳。在此组成和 0.2C 充放电时，其首次库仑效率分别为 81.9%（铜衬底）和 83.6%（镍衬底）。它们在室温下、1C 时的长期（100 次）可逆循环容量可达 790mAh/g（镍衬底）和 715mAh/g（铜衬底）；而在 70°C 下容量为 1269mAh/g（镍衬底）和 1018mAh/g（铜衬底），而且表现出更明显的容量随循环增加现象。

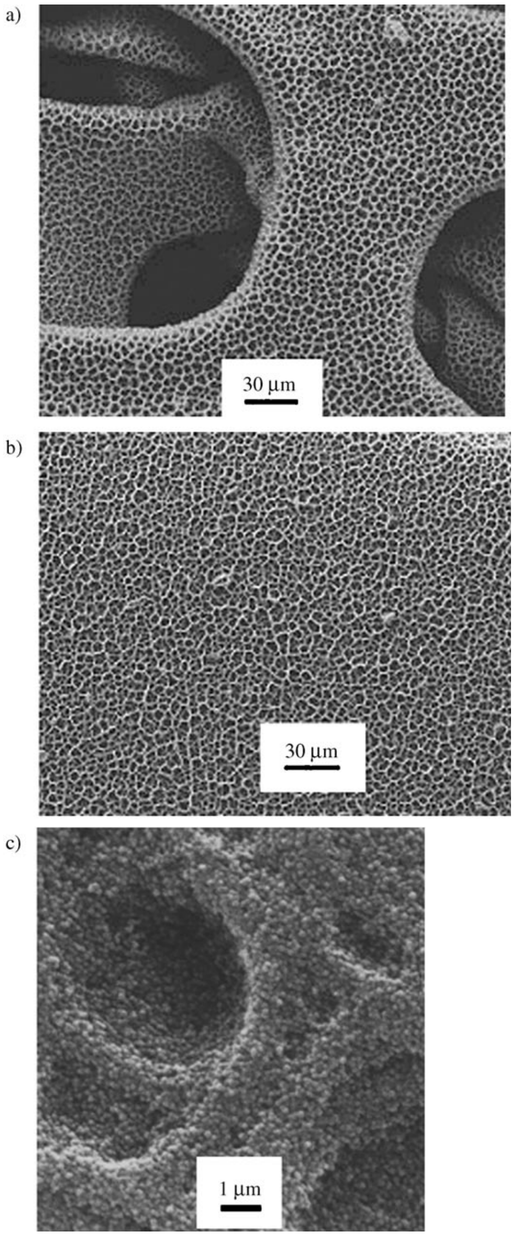

Figure 1. Scanning electron microscopy (SEM) images of the surface of a Li_2O/CoO (Li/Co = 1:1) composite thin film on a) nickel substrate and b) and c) Cu foil. All films were deposited at 235 °C in air.

Electrochemical Properties of CoO/Li_2O Electrodes

As shown in our previous paper,[18] the CoO/Li_2O (1:1) electrode on nickel foam substrate exhibits outstanding charge–discharge behavior. Figure 2 a shows the voltage profiles of the CoO/Li_2O (1:1) electrode on Cu foil at a constant charge–discharge rate of 0.2 C over a voltage range of 0.01–3.0 V. The charge–discharge curves are typical for a metal-oxide electrode with a distinct long plateau below 1 V followed by an inclined portion down to the cutoff voltage of 0.01 V in the first discharge process. According to Tarascon and co-workers,[23] the voltage plateau at 0.7 V is related the CoO → Co conversion process, whereas the sloping portion

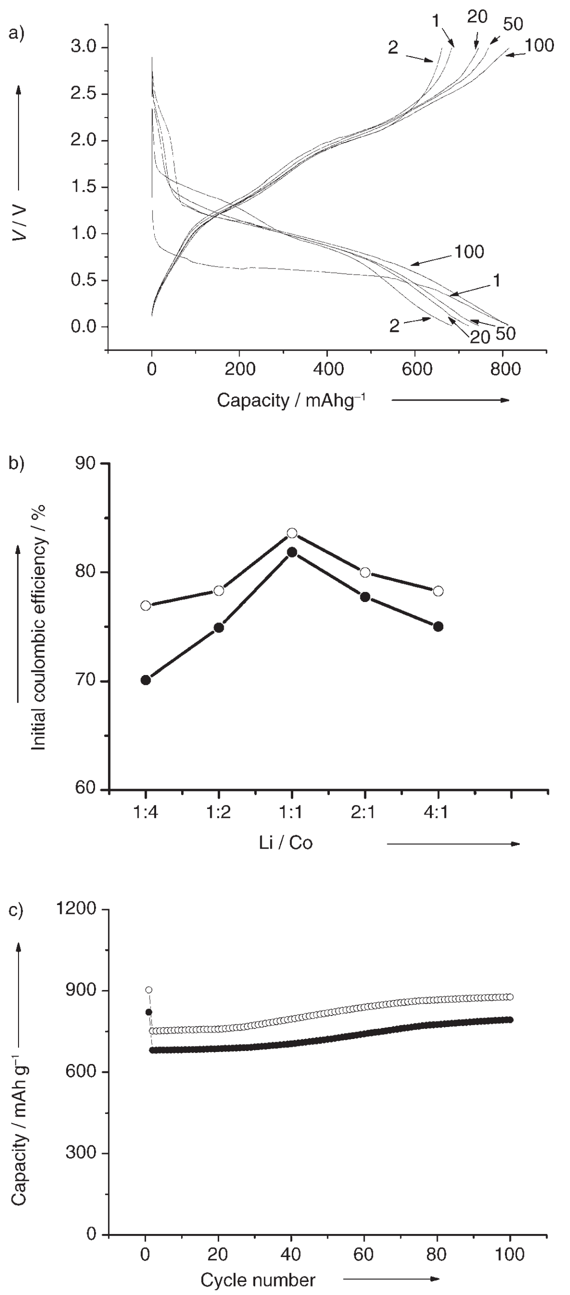

Figure 2. Electrochemical properties of the composite CoO/Li_2O (Li/Co = 1:1) films. a) Voltage profiles for CoO/Li_2O thin-film electrodes on Cu foil. The cycle numbers are indicated in the graph. b) Initial coulombic efficiency of the thin-film electrodes as a function of the Li/Co molar ratio. c) Capacity–cycle number relationship of the Li_2O/CoO thin-film electrodes/Li cells. The cells were cycled between 0.01 and 3.0 V at 0.2 C. ○ = Ni foam, ● = Cu foil.

down to 0.01 V is associated with the formation of predominantly a gel-like film and, in a very small fraction, an SEI layer on the particle surface. Furthermore, Co nanoparticles were formed during the discharge step; the other product of this conversion is Li_2O, that is, $CoO + 2Li \rightarrow Co + Li_2O$.

The discharge curves for subsequent cycles were lifted from the 0.7-V plateau of the first cycle to an inclined "plateau" at around 1.0 V, and the $CoO \rightarrow Co$ conversion became more and more inconspicuous with cycling. Meanwhile, the sloping portion down to 0.01 V, which is attributed to the formation of a gel-like film, became longer with cycle number.

On the charge curves of these composite films (Figure 2a herein and Figure 3a in reference [18]), there are two plateaus, one from 1.0 to 2.0 V and the other from 2.0 V to 2.5 V. As Tarascon and co-workers indicated that the gel-like film disappears when the voltage is higher than 2.0 V,[23] the capacity associated with the charge process from 0.01 to 2.0 V can be ascribed to the gradual dissolution of the gel-like film and the partial conversion process $Co \rightarrow CoO$. For the part above 2.0 V, the capacity should mainly correspond to the $Co \rightarrow CoO$ process. Besides, there is a clear increase in the slope of the charge curves above 2.5 V. The capacity associated with this voltage range can be at least partially attributed to the transition from Co^{2+} to Co^{3+}, because Co_3O_4 was detected after long-time cycling.[18] This transition can only occur in the presence of pre-added Li_2O, that is, $3CoO + Li_2O \rightarrow Co_3O_4 + 2Li$. We believe that further oxidation to Co_2O_3 should also be possible by a similar mechanism.

It was observed that both CoO/Li_2O (1:1) thin-film electrodes have rather high initial coulombic efficiencies. The film on Cu foil (Figure 2a) had an initial coulombic efficiency of 81.9%, which is a little lower than the 83.6% for the film on Ni foam.[18] Because an electrode with higher specific surface area is more accessible to the electrolyte molecules,[24] the use of the film on Ni foam as the electrode enhances the contact between electrolyte molecules and the electrode. Dou and co-workers[10,12] demonstrated that Ni addition can facilitate Li_2O decomposition, which is the reverse of the $CoO \rightarrow Co$ conversion, because of the catalytic activity of Ni. Similarly, this mechanism is probably responsible for the higher initial coulombic efficiency of thin films on Ni foam compared with that on dense Cu foil. This relationship also holds for films of other compositions or Li/Co ratios (Figure 2b), although maximum efficiency is attained at Li/Co = 1:1 for both series of films. Therefore, the substrate made from Ni plays an important role in reducing the initial irreversible capacity of the thin-film electrodes.

We previously reported that dense Li_2O-free thin films on Ni foam and Cu foil substrates show first-capacity losses of 31.4% and 38.2%, respectively,[18] which are much greater than the 16.4% and 18.1% for the CoO/Li_2O (1:1) thin films here (Figure 2b). This result suggests that irrespective of the type of substrate and thin-film morphology, the existence of pre-added Li_2O in deposited films may restrain the conversion-produced Li_2O from entering the irreversible SEI film during the first discharge process and thus increase the initial coulombic efficiency. The cycling performances of the CoO/Li_2O (1:1) electrodes on the two different substrates are compared in Figure 2c. It is obvious that the sample prepared on Ni foam performs better than that on Cu foil in that the former has a higher reversible capacity (877 mAh g^{-1}) and lower first-cycle irreversible capacity

(148 mAh g^{-1}) upon extended cycling (100 cycles). The better performance of thin films on Ni foam is attributed to the following. First, Ni foam has a porous structure that is beneficial for the electrolyte to soak into active particles. This character ensures both electronic and ionic conductivity during the charge–discharge processes. Second, as mentioned above, the Ni substrate may catalyze the Li_2O decomposition during the first charge process.[10,12] Another beneficial factor could be the coarseness of the surface, which strengthens the adhesion between the layer and current collector and maintains the structural integrity of the electrode during cycling.

To gain further understanding of the influence of the substrate, the impedance spectra of the CoO/Li_2O (1:1)/Li cells on Cu foil and Ni substrate at different cycle numbers were recorded (Figure 3). They were all obtained in a fully discharged state at an open-circuit voltage of 0.01 V. The impedance spectra of the cells are typical for the ESD-derived film electrode, showing only one clear semicircle[25] in the intermediate-frequency range together with a small overlapping arc in the high-frequency end. It is clear that the impedance of the cell with the CoO/Li_2O (1:1) electrode on nickel foam is significantly less than that on Cu foil, which can be attributed to a larger contact area in the former case. This relationship can explain the higher capacity measured for the electrode on Ni foam (Figure 2c). Also, the cell resistance gradually decreased with an increase in cycle number, which is presumably due to a decrease in particle size with cycling.

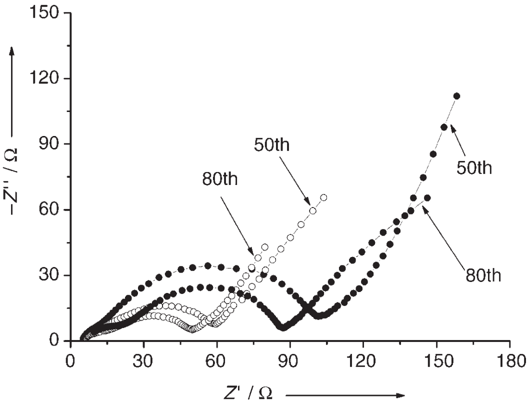

Figure 3. AC impedance spectra of the CoO/Li_2O (Li/Co = 1:1)/Li cell at different cycles. The cells were discharged to 0.01 V at a discharge rate of 0.2 C. The cycle numbers are indicated in the graph. The substrates were Ni foam (○) and Cu foil (●).

Effect of the Molar Ratio of Li to Co

Figure 4 shows the evolution of the reversible capacity of thin-film electrodes on Cu foil and Ni foam with five different Li/Co ratios. The tested cells were all cycled at 0.2 C. The two series on different substrates displayed a similar relationship with the Li/Co ratio, although the electrodes on Ni foam exhibited a slightly higher capacity. Irrespective of the substrate, the capacity increased with an increase in the Li/Co ratio; when the ratio reached 1:1, the capacity was at a maximum of 850 mAh g^{-1} for the film on Ni foam and 750 mAh g^{-1} for the film on Cu foil. When the Li/Co ratio was increased further, a fast capacity fading was clearly observed. As discussed before, the discharge of metal-oxide electrodes towards lithium involves two distinct processes: the conversion between CoO and Co and the formation of a gel-like film on the surface.[9] The first process induces a volume variation. The second forms a gel-like film that can restrain the nano-Co particles from aggregating and relieve volumetric variation. In the Li_2O/CoO composite electrodes, Li_2O may act as a volume buffer because it is dispersed uniformly in the deposited films. During the conversion process, the volume change can be effectively absorbed by the Li_2O matrix, preventing the crumbling of the electrode and retaining good cyclability. Morimoto et al. obtained similar results with mechanically milled $SnO/B_2O_3/P_2O_5$ composites with and without Li_2O.[26] Additionally, the Li_2O-loaded electrode increases the interface between the particles and thus more gel-like films are formed during the discharge process.[27] As a result, the discharge capacity increases with increasing Li_2O content. However, when the Li_2O loading reaches a certain limit in the deposited electrodes, the poor electronic conductivity of Li_2O may obstruct the contact between neighboring active particles and induce a loss of electrical contact between them, resulting in rapid capacity fading.

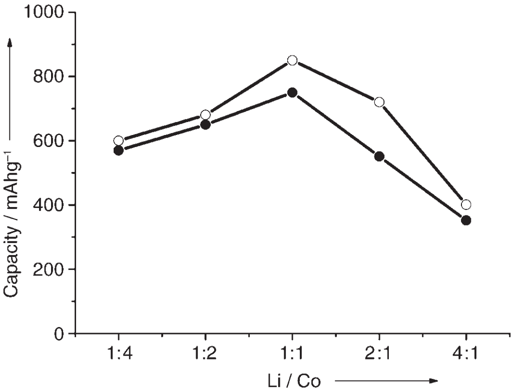

Figure 4. Reversible capacity of CoO/Li_2O thin-film electrodes as a function of Li/Co molar ratio. The cells were cycled between 0.01 and 3.0 V at 0.2 C. The substrates were Ni foam (○) and Cu foil (●).

With the optimized composition, that is, Li/Co = 1:1, the rate capability of the cells on Ni foam and on Cu foil substrates was evaluated. Figure 5 shows the specific capacity of CoO/Li_2O (1:1)/Li cells as a function of charging rate. The capacity decreased with an increase in charging rate for all the samples, suggesting that the polarization due to the electrical resistance of the electrode increases with an increase in charging rate. Furthermore, at the same charging rate, the electrode on Ni foam has the higher capacity. Therefore, the increase in surface area of active materials promotes an electrochemical lithium reaction with the composite active

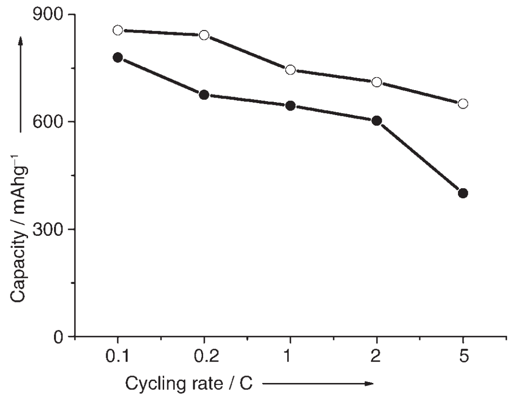

Figure 5. Rate capability of CoO/Li_2O (Li/Co = 1:1)/Li cells. The cells were cycled between 0.01 and 3 V. The substrates were Ni foam (○) and Cu foil (●).

layer, probably due to a suppression of the polarization per unit surface area.

Effect of the Temperature

To investigate the influence of temperature on cycling performance, Li_2O/CoO composite films with the optimal composition Li/Co = 1:1 on Ni foam and Cu foil were chosen. All cells were cycled at a rate of 1 C between 0.01 and 3.0 V at 25 and 70 °C. The cycling performances of the composite thin-film electrodes are shown in Figure 6 and were all excellent. The capacity of the thin-film electrodes on Ni foam was substantially higher than those on Cu foil, especially at high temperature (70 °C). All electrodes exhibited increased capacity upon cycling, which is a direct result of the decomposition of the electrolyte driven by the transition-metal nanoparticles.[27] The capacities at 70 °C were all larger than the theoretical value (715 mAh g^{-1}). More specifically, as shown in the voltage profiles of cells cycled at 70 °C (Figure 7), the sample on Ni foam (Figure 7 a) increased its capacity from 814 (2nd) to 1266 mAh g^{-1} (100th) at 70 °C, which is a corresponding capacity increase of 0.56 % per cycle. The sample on Cu foil (Figure 7 b) gave a slightly lower capacity, offering 806 (2nd) to 1018 mAh g^{-1} (100th).

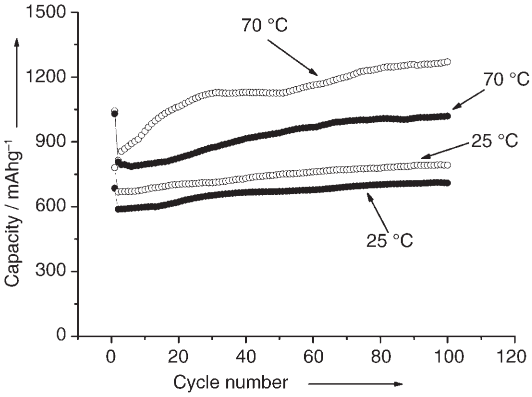

Figure 6. Capacity–cycle number relationship of Li_2O/CoO (Li/Co = 1:1)/Li cells at 25 and 70 °C. ○ = Ni foam, ● = Cu foil.

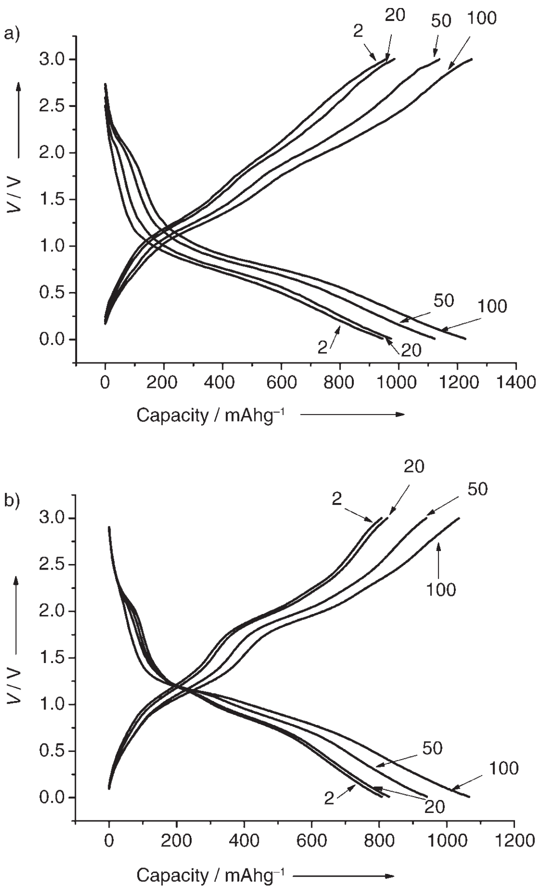

Figure 7. Voltage profiles for CoO/Li_2O (Li/Co = 1:1)/Li cells cycled at 1 C and 70 °C. The substrates were a) Ni foam and b) Cu foil. The cycle numbers are indicated in the graphs.

The discharge curves of both electrodes at 70 °C (Figure 7) have a shorter plateau but longer sloping part, in contrast to the room-temperature curves (Figure 2 a). This implies that the formation of the gel-like film is dominant over the CoO → Co conversion at higher temperature. This is in agreement with the opinion of Tarascon and co-workers that the formation of the gel-like film is governed by kinetics and is naturally more significant at higher temperatures.[27] During the first discharge, the Co nanoparticles form first, then the gel-like film (shell) envelopes the Co metal (core). The gel-like film contains, among others, organic oligomer chains of poly(ethylene oxide) ($(CH_2CH_2O)_n$; $n \leq 9$) with H, CH_3, or C_2H_5 as terminal groups. Inorganic components such as Li_2CO_3, $ROCO_2Li$, and RCO_2Li are also present.[28] The organic components contribute to reversible capacity, whereas the inorganic components are irreversible. In a comparison of the electrodes on the two types of substrates, the samples on Ni foam showed better performance. We believe that the Ni substrate cooperates with Co to catalyze the decomposition of the electrolyte, resulting in the formation of more gel-like films, thus leading to more "extra capacity".

Finally, the capacity of the CoO/Li_2O films did not rise forever but reached a maximum after hundreds of cycles.

Typically, the maximum capacity appeared after about 300 cycles at 25 °C and 150 cycles at 70 °C. Besides, as already indicated in our previous paper,[18] the nickel foam substrate may contribute to about 10 % of the total capacity owing to partial surface oxidation. This contribution to capacity was subtracted in the data presented above. A similar comparative study suggests that the Cu foil substrate does not participate in the electrochemical reactions and hence does not contribute to the capacity.

Conclusions

We have succeeded in fabricating highly porous reticular Li_2O/CoO composite thin films not only on dense substrate (Cu foil) but also on porous substrate (Ni foam). The thin-film electrodes present excellent reversible capacity despite the absence of carbon. The molar ratio of Li to Co plays a crucial role on the electrochemical performance of the thin-film electrodes. The Li_2O component disperses uniformly in the CoO bulk and acts as a buffer to decrease volume change during cycling. The addition of Li_2O also helps to improve the initial coulombic efficiency. It was found that the optimal Li/Co molar ratio for the best electrochemical performance is 1:1. Transition-metal-oxide electrodes form a gel-like film on their surface during cycling. The higher discharge capacity of thin-film electrodes on Ni foam suggests that the amount of gel-like film is affected by the nature and specific surface area of the current collector. The Ni substrate plays a double role: it catalyzes the Li_2O decomposition during the first charge process and improves the initial coulombic efficiency, and it cooperates with the nano-Co to catalyze the formation of the gel-like film during cycling. Ni foam, with its porous structure and coarse surface texture, has proved to be a good candidate for current collectors.

Experimental Section

The films of CoO/Li_2O were prepared by ESD. Details about the experimental procedure are described in previous papers.[14,15] A distance of 2–3 cm was kept between the needle and the substrate. The applied voltage was 11–13 kV. Lithium acetate dihydrate (0.0255 g, 0.25 mmol; 99 %) and cobalt acetate tetrahydrate (0.6226 g, 0.25 mmol; 99 %) were dissolved in pure butyl carbitol ($CH_3(CH_2)_3OCH_2OCH_2CH_2OH$; 50 mL) for film deposition. To investigate the effect of the molar ratio of Li to Co in solution, we prepared five precursor solutions with Li/Co molar ratios of 1:4, 1:2, 1:1, 2:1, and 4:1, with the Co concentration kept constant at 0.005 M. The precursor solution was pumped through the metal capillary nozzle at a rate of about 4 $mL\,h^{-1}$. The nickel foam (0.2 mm in thickness, 14 mm in diameter) or Cu foil substrate (0.1 mm in thickness, 14 mm in diameter) were heated at 235 °C. The deposition lasted 90 min, and the mass of the deposited layer was controlled at about 2 $mg\,cm^{-2}$. Film deposition took place under ambient atmosphere.

The thin films were characterized by SEM (HITACHI X-650) and XRD (Philips X'Pert PRO SUPER with $Cu_{K\alpha 1}$ radiation, $\lambda = 1.541$ Å), and the thin-film electrodes were assembled into coin-type cells (2032) with a Li electrode and LB 302 electrolyte (1 M $LiPF_6$ in ethylene carbonate and diethyl carbonate (EC/DEC = 1:1 v/v)) in an argon-filled glove box (MBraun Labmaster 130). Electrochemical measurements were carried out with a battery test system (NEWARE BTS-610). They were cycled at a c rate of 0.1–5 C in the voltage range between 3.0 and 0.01 V. The impedance spectra of the cells were recorded with a CHI 604B Electrochemical Workstation in the frequency range of 0.01–100 kHz.

Acknowledgements

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