

Short communication

Discharge characteristics of silver/lithium cobalt oxide cell for medical application

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Abstract

The discharge capacity and storage characteristics of Ag/LiCoO₂ and Cu/LiCoO₂ cells are studied. The discharge capacity of the Ag/LiCoO₂ cell is better than that of the Cu/LiCoO₂ cell. The Ag/LiCoO₂ cell gives a maximum discharge capacity of 190 mAh g⁻¹. The structure of lithium cobalt oxide changes from trigonal to monoclinic ($a = 4.61 \text{ \AA}$, $b = 2.81 \text{ \AA}$, $c = 4.80 \text{ \AA}$, $\beta = 122.6^\circ$) system as the content of lithium is decreased. The Ag/LiCoO₂ cell shows good storage properties, there is little decrease in discharge capacity after 7 days at room temperature. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lithium cell; Discharge capacity; Self-discharge

1. Introduction

During the last two decades, considerable interest has been focused on the development of batteries with high specific energy and good storage characteristics [1–3]. Lithium primary batteries have been used as high-performance cells [4–7]. Despite rapid advances in this technology, the batteries do not satisfy the need of recent micro-medical appliances, such as endoscopic microcapsules and drug-delivery systems [8,9]. The power source requirements for implantable devices must meet safety standards and have high rate capability, reliability and good storage life in addition to high specific energy. Lithium-ion secondary batteries are usually composed of lithiated transition metal oxide as the positive electrode and graphite material as the negative electrode. These batteries are safer than lithium primary and secondary batteries because they do not use lithium metal electrodes. The discharge capacity of the present lithium-ion battery is limited, however, in order to maintain good cycling performance.

In this paper, we have assembled two types of Cu/LiCoO₂ and Ag/LiCoO₂ cells for use as primary lithium cells with high specific energy and good safety. The maximum discharge and storage capacity of the cells are investigated.

2. Experimental

2.1. Materials and electrodes

A silver anode was prepared by coating silver on a copper substrate by sputtering (Sam Won Vac., SWSE-42TS), and LiCoO₂ coated on aluminum foil was used as a cathode. This cathode was made from LiCoO₂ active materials (SEMI Co.), acetylene black conductor, and poly(vinylidene fluoride) binder slurry. The mixture was cast on aluminum foil by the doctor-blade method. Celgard 2400 polypropylene film and non-aqueous organic solution (1 M LiPF₆) were used as a separator and an electrolyte, respectively.

2.2. Cell assembly

Cu/LiCoO₂ and Ag/LiCoO₂ cells were assembled in the 0 V discharged state while the Li/LiCoO₂ cell was assembled in the 3.0 V discharged state. All cells were enveloped in an aluminum plastic bag and sealed under vacuum in a dry room (dew point: -70°C).

2.3. Cell test and analysis

All cells prepared in this study were tested by a galvanostatic method using a Maccor cycle-tester (model No. 4000 GENT). The cells were charged to 4.5 V and discharged to 2.7 V under constant current. Some cells were stored after

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charging for several days at room temperature to investigate their self-discharge characteristics. The structure of LiCoO_2 before and after cycling test was analyzed by X-ray diffraction (XRD, model No. RINT/DMAX-2500, Rigaku). The depth profile of the silver coated on copper was observed by means of Auger electron spectroscopy (AES, model No. PHI-670).

3. Results and discussion

3.1. Depth profile of Ag layer coated on Cu substrate

The depth profile of the silver layer coated on the copper substrate is shown in Fig. 1. The silver metal was densely and uniformly deposited on the copper substrate. The sputtering rate was 100 \AA SiO_2 per min. The thickness of silver was about 300 \AA . Although, oxygen molecules were found at the surface of the copper, the adhesion between silver and copper was good. Therefore, the silver film could not be easily peeled off the copper substrate. As a result, the interfacial contact resistance between the two metals was negligible.

3.2. XRD analysis of LiCoO_2

The X-ray diffraction patterns of fully lithiated cobalt oxide (LiCoO_2) and partially delithiated cobalt oxide ($\text{Li}_{1-x}\text{CoO}_2$) are shown in Fig. 2(a) and (b), respectively. The conventional crystal structure of LiCoO_2 has trigonal symmetry (space group $R\bar{3}m$) and deviates from ideal, cubic close-packing by the magnitude of the crystallographic c/a ratio, for which cubic symmetry is 4.90 [10]. The values of the lattice parameters a and c for fully lithiated cobalt oxide

electrode are 2.84 and 13.87 \AA , respectively. The magnitude of the c/a ratio is 4.88 for this electrode, which is larger than the reported value of 4.99 [11] and the value of 4.90 for the ideal layered configuration of LiCoO_2 [10]. This may be due to the process of lithiation in the LiCoO_2 electrode during the sample preparation.

Amatucci et al. [12] have reported that the trigonal symmetry of LiCoO_2 is transformed to the monoclinic form by the delithiation. The lattice parameters a , b , and c for delithiated cobalt oxide $\text{Li}_{0.21}\text{CoO}_2$ are 4.83, 2.82, and 4.96 \AA , respectively. In the present study, the lattice parameters a , b and c for delithiated cobalt oxide electrode are 4.61, 2.81, and 4.80 \AA , respectively.

3.3. Comparison of Cu/LiCoO_2 and Ag/LiCoO_2 cells

The voltage profiles of Cu/LiCoO_2 and Ag/LiCoO_2 cells are presented in Fig. 3. The Ag/LiCoO_2 cell shows excellent cycling efficiency and specific discharge capacity compared with the Cu/LiCoO_2 cell. This behavior may be attributed to a good reversibility of silver and lithium. Although, lithium extracted from the LiCoO_2 electrode is successfully deposited on copper, it is not completely inserted into the LiCoO_2 electrode. A large amount of lithium remains on the copper surface. The lithium deposited during charging reacts chemically with organic electrolytes. The cycling efficiency (CE) of lithium is defined by the following equation [13]:

$$\text{cycling efficiency} = 100 \times \frac{Q_p}{Q_s} \quad (1)$$

where Q_p is the amount of electricity required to plate lithium and Q_s is the amount of electricity required to strip lithium.

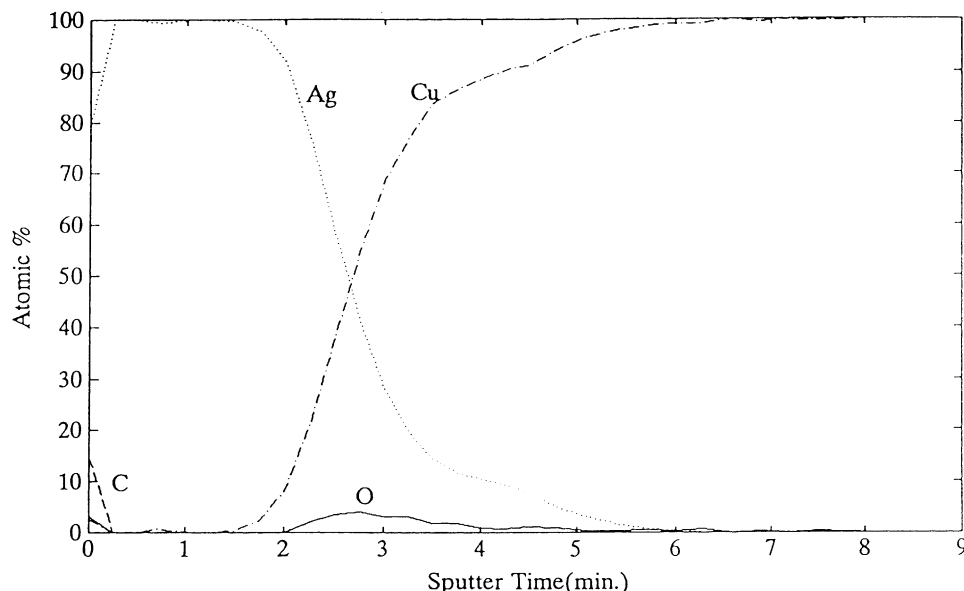


Fig. 1. AES depth profile analysis of silver coated on copper substrate.

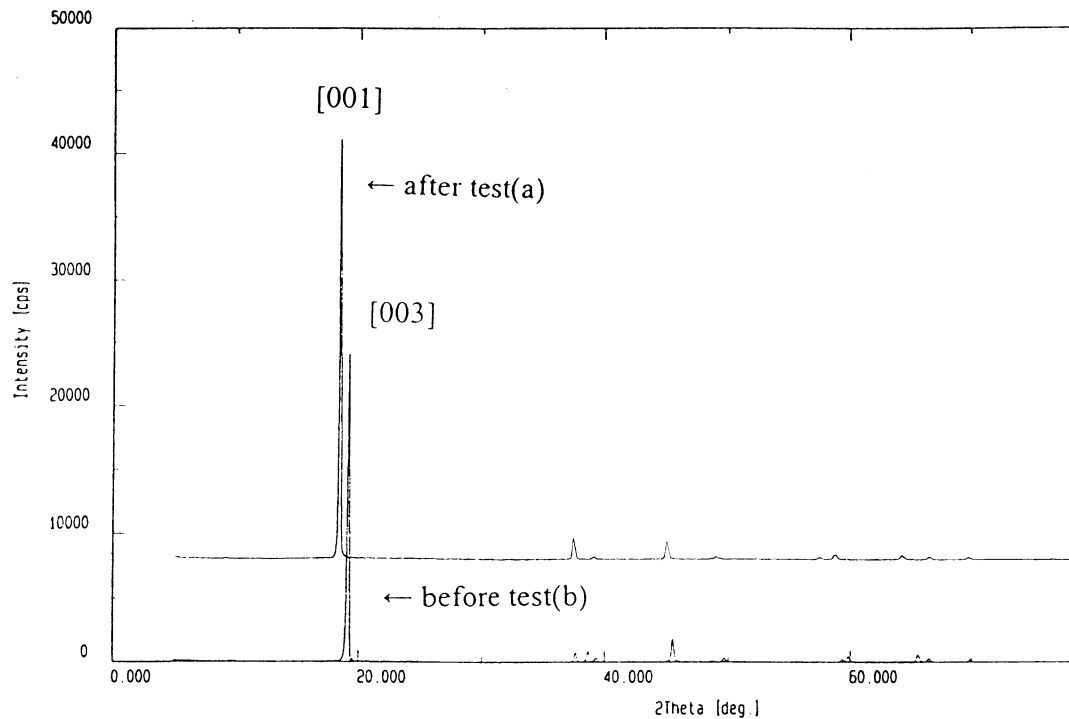
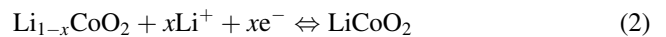


Fig. 2. XRD patterns of LiCoO₂ cathode (a) after and (b) before cell test.

Similar results were obtained in propylene carbonate–dimethoxy ethane (PC–DME) electrolyte. As shown in Fig. 4, the copper electrode displays poor cycling performance in PC–DME electrolyte than in ethylene carbonate–ethyl methyl carbonate (EC–EMC) electrolyte. It is expected that the cycling efficiency of lithium depends on the substrate as well as the electrolyte used. Generally, the oxidative stability of organic esters is higher than that of ethers. Therefore, the poor cycling in PC–DME electrolyte may be due to the low stability of the electrolyte.

3.4. Cycling performance of Ag/LiCoO₂ cell

The overall reaction of LiCoO₂ is given by Eq. (2) and the theoretical capacity of LiCoO₂ is 273 mAh g⁻¹.



As seen in Fig. 5, the calculated charge capacity of LiCoO₂ on the first cycle is 210 mAh g⁻¹, when x is 0.73. Ohzuku [14] has reported that the discharge capacity of the Li/LiCoO₂ cell is 194 mAh g⁻¹ at 4.6 V and 0.17 mA cm⁻²

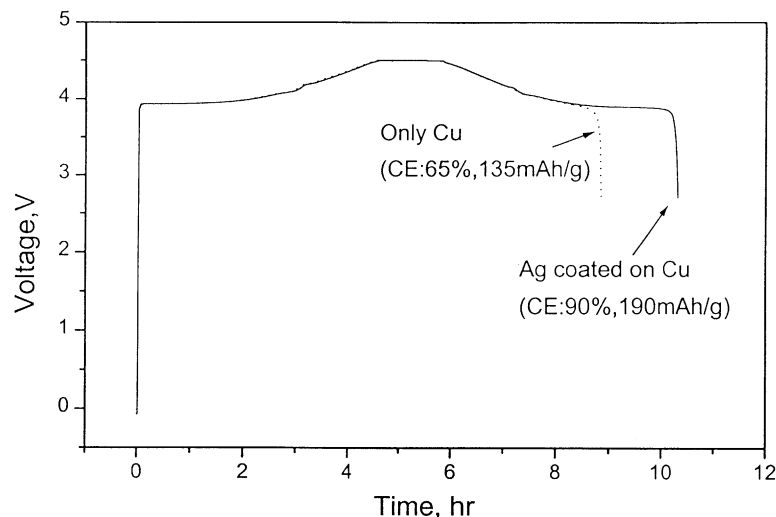


Fig. 3. Voltage profiles of Li-free/LiCoO₂ cell at room temperature (current density: 0.67 mA cm⁻², electrolyte: 1 M LiPF₆/EC: EMC).

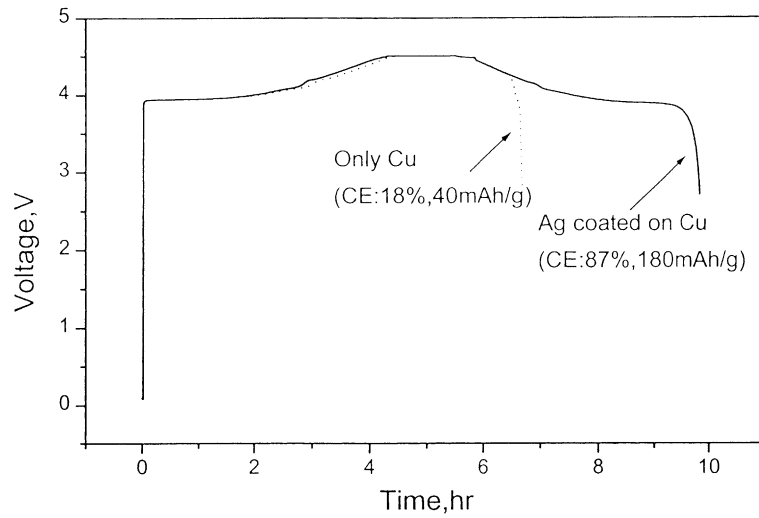


Fig. 4. Voltage profiles of Li-free/LiCoO₂ cell at room temperature (current density: 0.67 mA cm⁻², electrolyte: 1 M LiPF₆/PC: DME).

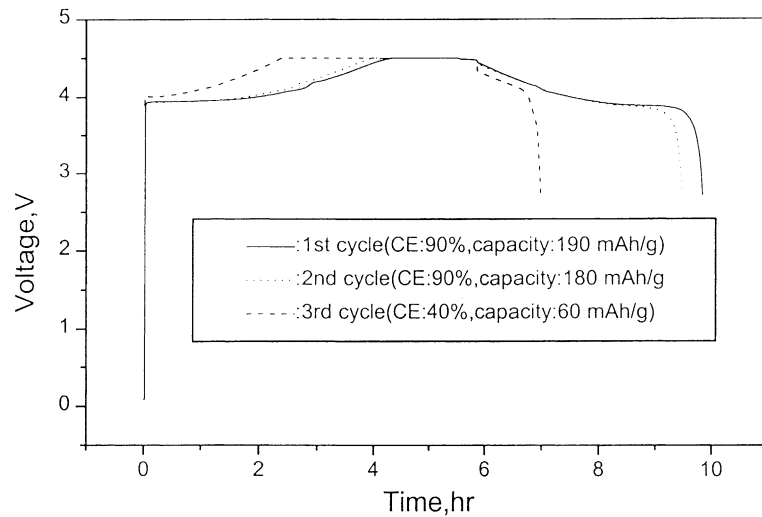


Fig. 5. Voltage profiles of Cu/Ag/LiCoO₂ cell with cycle number (current density: 0.67 mA cm⁻², electrolyte: 1 M LiPF₆/EC: EMC).

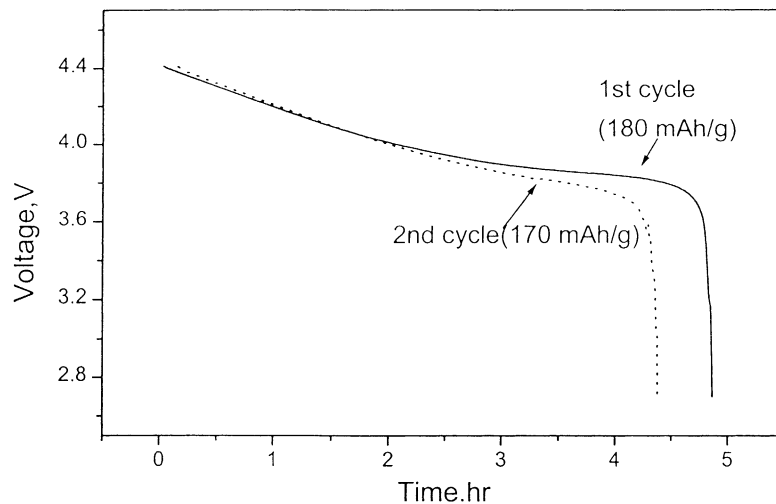


Fig. 6. Self-discharge curves of Cu/Ag/LiCoO₂ cell after 7 days (electrolyte: 1 M LiPF₆/EC: EMC; current density: 0.67 mA cm⁻²).

discharging conditions in 1 M LiClO₄/PC electrolyte. Although, for our LiCoO₂ electrode, the rate of charge and discharge is much faster (four times), the discharge capacity is similar to Ohzuku's results. The discharge capacity decreases slightly on the second cycle but drops to 60 mAh g⁻¹ on the third cycle owing to the structural change of LiCoO₂. The average working voltage is about 4.1 V irrespective of cycle number.

3.5. Self-discharge of Ag/LiCoO₂ cell

The Ag/LiCoO₂ cell was charged to 4.5 V, and then stored for 7 days at room temperature. The self-discharge curves for first and second cycles are shown in Fig. 6. The discharge capacity decreases slightly compared with the initial capacity after 7 days. Therefore, this cell is suitable for electronic devices and micro-medical appliances.

Self-discharge capacity depends on the reactivity of lithium, moisture and oxygen in electrolyte [15]. Although, this cell does not contain lithium metal as an anode in the initial state, the silver anode is transformed to a Ag–Li alloy after charging. Then, this anode may react with organic electrolyte in the same way as lithium metal.

Another factor in self-discharge is the structural change of the LiCoO₂ electrode. The LiCoO₂ electrode is usually more sensitive to self-discharge than any other transition metal oxide electrode such as LiMn₂O₄, V₂O₅ and MnO₂. Studies of relationship between self-discharge capacity and other transition metal electrodes, as well as the electrolyte, are in progress.

4. Conclusions

The Ag/LiCoO₂ cell prepared in this study implies the possibility of an implantable battery that exhibits desirable properties such as high discharge capacity and good self-discharge capacity. This cell has a discharge capacity of 190 mAh g⁻¹, and can be sustained for 7 days. In addition to

these positive effects, a cell without lithium is safer. Further work are in progress to minimize self-discharge capacity and hence, develop implantable batteries with greater reliability.

Acknowledgements

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