

Anodic polarization behavior of copper in propylene carbonate

Jin Kawakita^{a,*}, Kenzo Kobayashi^b

^aNational Research Institute for Metals, 1-2-1 Sengen, Tsukuba-shi, Ibaraki 305-0047, Japan

^bDepartment of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, Kouhoku-ku, Yokohama 223-8522, Japan

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Abstract

Anodic polarization behavior of copper in propylene carbonate was investigated using electrochemical measurements, microscopic observations, elemental and gravimetric analyses. These results exhibited that anodic polarization of copper brought about oxidative dissolution of the metal substrate in competition with decomposition of the electrolyte on the metal surface. A reaction mechanism for oxidative dissolution was proposed with respect to both the charge transferring and the geometric form. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Lithium-ion secondary batteries are used mostly as the power sources for the portable phones and the mobile computers because of their high energy density per weight and volume. They have a distinctive feature that lithium ion moves between the electrode material and the aprotic organic solvent during the discharge and charge processes accompanying electron transfer [1].

Some kinds of side reaction were reported to take place on the electrode when the battery was over-charged or over-discharged. They were decomposition of the electrolyte [2–4], irreversible phase change of the electrode material [5–8], and electro-deposition of metallic lithium on the electrode surface [9].

In addition, there is corrosion of the current collector, which plays an important role in exchanging the electron between the electrode material and the external circuit. Although metals are probably suitable as a current collector for the requirement of high conductivity, it may be subjected to corrosion environment during the discharge and charge cycle. When the battery is charged, the potential of the positive electrode increases above 4.0 V (versus Li/Li⁺ standard potential). In such high potential, i.e. under a highly oxidative condition, corrosion of most metals is inevitable. In general, aluminum (Al) is a corrosion-resistant metal in air and neutral water environments without aggressive

materials, because the surface of Al itself is covered with a protective oxide film. It was expected that Al retained this character to some extent even in the non-aqueous electrolyte. Therefore, Al has been used as a current collector for the positive electrode in the commercial lithium-ion batteries. However, replacement of water with an inorganic solvent showed, that are not seen in usual aqueous solutions, as reported by many researchers [10–19].

On the other hand, even if the negative electrode is over-discharged, the electrode potential is relatively low, i.e. about 1.5 V at most. Therefore, corrosion of the current collector is not feasible to occur and a commercial lithium-ion cell adopts metallic copper (Cu). The negative electrode, however, may reach a high potential enough to be subjected to corrosion at the last period of the discharge process, if the positive electrode accepts a compound with high potential to obtain higher energy. From this viewpoint, anodic polarization behavior of copper has been reported in literatures [20,21]. Furthermore, environmentally assisted cracking (EAC) was found to occur at the copper electrode when the cycle of lithium deposition and dissolution was repeated under the bending stress [22].

In this study, we have aimed to elucidate the reaction mechanism of the phenomenon, which takes place on the current collector of the negative electrode during the discharge of the lithium-ion cell. Anodic polarization behavior of pure Cu in lithium perchlorate/propylene carbonate (LiClO₄/PC) solution was investigated using polarization, electrochemical quartz crystal microbalance (EQCM), field emission scanning electron microscopy (FE-SEM) and XPS

* Corresponding author. Tel.: +81-298-59-2124; fax: +81-298-59101.
E-mail address: kawakita@nrim.go.jp (J. Kawakita).

measurements. The EQCM is a gravimetry technique connected with the electrochemical measurement. The FE-SEM was adopted for the microscopic observation of the surface and the cross-section. The X-ray photoelectron spectroscopy was used for the elemental analysis of the surface state for Cu.

2. Experimental

A specimen of Cu (99.99% in purity) was cut into small pieces with dimensions of 10 mm × 40 mm × 0.2 mm, and degreased by ultra-sonication in acetone for 30 min and dried in a cool air stream.

The specimen of Cu was electropolished at an anodic constant voltage of 2.0 V in a concentrated phosphoric acid solution for around 15 min to obtain a mirror-like surface. Immediately after electropolishing, the specimen was rinsed out thoroughly in the 10% phosphoric acid solution and in flowing water to remove the sticky fluid attached to the surface of the specimen. Finally, the specimens were dried in a cool air stream.

Electrochemical measurements were carried out in a cylindrical glass cell with three electrodes. An electropolished specimen of Cu and a foil of Cu were used as the working and the counter electrodes, respectively. The reference electrode was a metallic lithium rod (Aldrich, 3.2 mm in diameter), which was embedded in a glass tube with a glass-wool membrane at one end and filled with the electrolyte. The PC solution containing 1 mol dm⁻³ LiClO₄ (Mitsubishi Chemical, water content <20 ppm) was adopted as the electrolyte. Potentiodynamic method was performed at a constant sweep rate of 50 mV s⁻¹ from the rest potential to 10 V with an aid of a galvanostat/potentiostat (Hokuto Denko, HA-301) connected with a function generator (Hokuto Denko, HB-104). In addition, galvanostatic polarization was carried out at an anodic current density of 0.1 to 1.0 mA cm⁻². All the procedures were conducted in a glove box filled with argon gas. In this paper, the electrode potential is represented as volt versus Li/Li⁺ standard.

The surface and the cross-section of the Cu specimen were observed before and after the electrochemical measurement by FE-SEM (Hitachi S-4700). For preparation of the cross-section, the specimen was embedded into epoxy resin in a capsule, and was sharpened and trimmed at an end with a glass knife followed by a diamond one to expose the cross-section by removal of the resin.

The surface of the Cu specimen was characterized by XPS using a JEOL apparatus (JPS-9000MC) with an Mg K α anode X-ray source with the primary beam energy of 15 kV and an electron current of 20 mA.

The weight change of the specimen during galvanostatically anodic polarization was determined by EQCM using Hokuto Denko apparatus (HQ-302) connected with the galvanostat. The working electrode was prepared by evaporation of Cu on an AT cut quartz disc by RF sputtering

with a target metal of Cu (99.99%, Furuuchi Chemical) under a trace of argon gas. The original resonance frequency of the quartz was 6 MHz. The evaporated Cu film had the geometric surface area of 1.327 cm² and the thickness of approximately some hundred nano-meters, which was calculated by the average accumulation rate (70 nm min⁻¹). Except for the working electrode, the EQCM experiment was carried out using the same components of the electrochemical cell as described above.

3. Results and discussion

An anodic polarization curve of the Cu specimen in the LiClO₄/PC solution at 50 mV s⁻¹ is shown in Fig. 1. An extremely low current began to flow at an electrode potential of 2.6 V and increased slightly. Relatively high current rose continuously with polarization to the higher potential over 3.55 V. These results are explained by occurrence of an additional reaction overlapped on the original one. No obvious peaks on the curve correspond to a lack of the simple diffusion-limited process. Accordingly, it is supposed that the anodic polarization of Cu caused oxidative dissolution of the metal substrate, followed by decomposition of the electrolyte on the metal surface rather than formation of the solid compound.

The result of galvanostatic polarization of the Cu anode in the LiClO₄/PC solution indicated the same tendency at a current density of 0.1 to 1.0 mA cm⁻². Typical potential curve is shown in Fig. 2 as a function of polarization time at 0.1 mA cm⁻². The abscissa shows the duration time when the circuit was closed. In the early stage of polarization, a rapid increase in the electrode potential was caused by oxidative dissolution of the Cu substrate. Actually, this

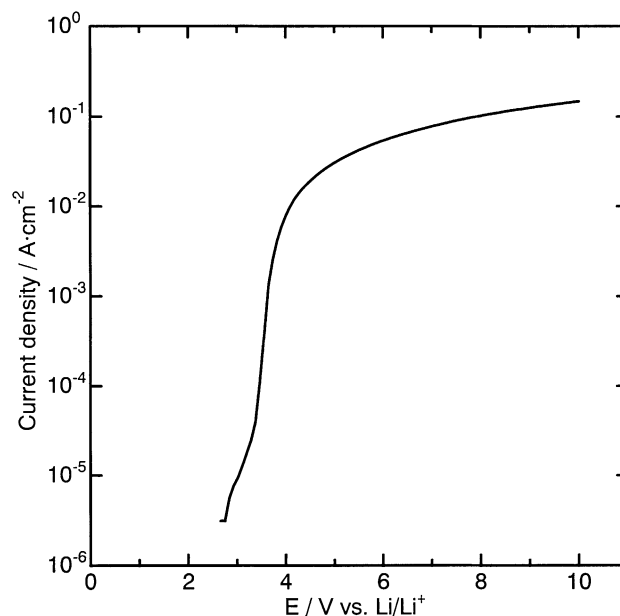


Fig. 1. Anodic polarization curve of Cu in LiClO₄/PC at 50 mV s⁻¹.

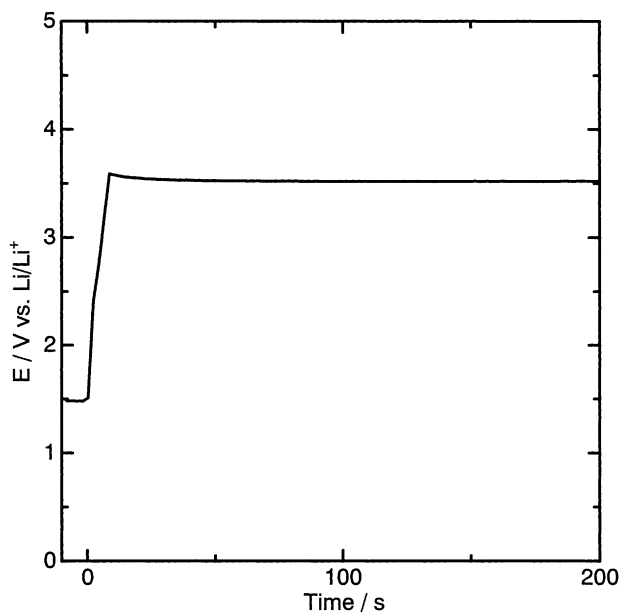


Fig. 2. Electrode potential of Cu as a function of polarization time in LiClO_4/PC at 0.1 mA cm^{-2} .

process started at a bending point near 2.5 V in the increasing line, taking into account the result of the anodic polarization (Fig. 1). After reaching 3.6 V, the electrode potential dropped gradually and then kept almost constant near 3.5 V, indicating occurrence of a competitive reaction such as decomposition of the electrolyte on the electrode as well as continued oxidative dissolution of the Cu substrate. Presumably, the gradual decrease in potential might be a phenomenon during the induction period before the occurrence ratio of each reaction reached the steady-state value.

Fig. 3 shows SEM images of the surface of the Cu specimen after galvanostatic polarization in the LiClO_4/PC solution at 0.1 mA cm^{-2} for 300 s. There were numerous etch pits at the whole surface, as seen especially in the upper image (Fig. 3a), and grain boundaries were observed clearly. Furthermore, no obvious solid corrosion products could be seen on the Cu surface. A section of the upper image is magnified and shown in the lower one (Fig. 3b). Almost all the etch pits had a characteristic shape, which seemed that a hole with the square aperture area advanced toward the inside of the substrate. Even in the comparatively microscopic view, the solid corrosion product was not observed on the surface and in the pit. These results imply that the general corrosion took place on the Cu surface together with dissolution of the copper cation formed by electrochemical oxidation of the Cu substrate. The cross-sectional SEM images of the galvanostatically polarized Cu specimen are shown in Fig. 4. The characteristic etch pits were also observed at the interface between the Cu substrate and the resin used for embedding. In addition, some defective parts could be seen inside of the Cu substrate, situated at a distance from the interface. These results suppose that the

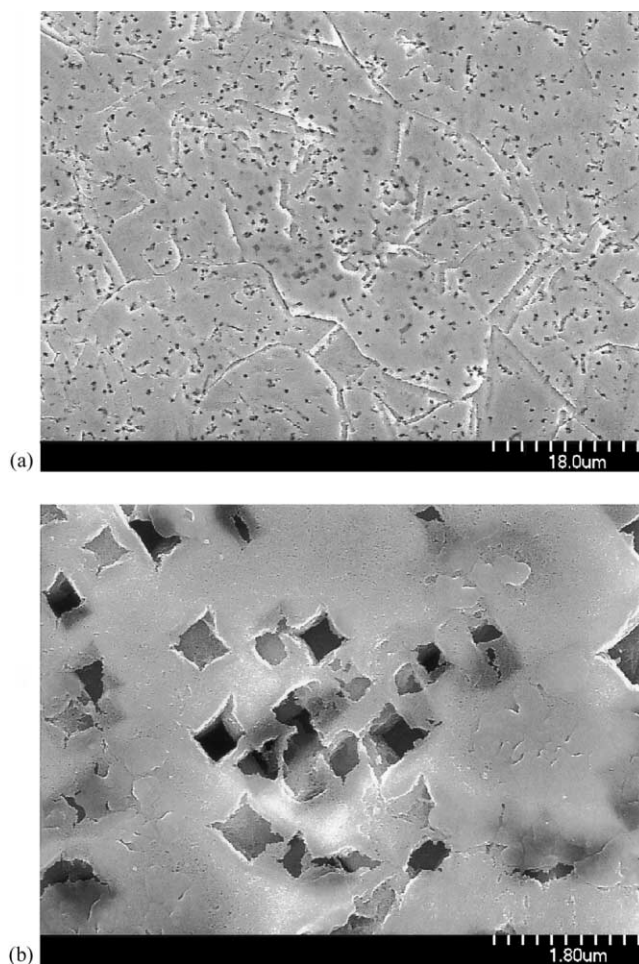


Fig. 3. SEM images of surface of Cu after polarization in LiClO_4/PC at 1.0 mA cm^{-2} for 300 s: (a) 1000 \times ; (b) 10,000 \times .

corrosion reaction proceeded not only toward the simple internal direction but also toward the specific one. This was because the corrosion direction would depend on the crystallographic orientation of the copper grain. Furthermore, any solid corrosion product did not appear in both the etch pits and the defects, indicating that anodic polarization of copper in propylene carbonate causes a typical activated dissolution reaction.

XPS spectra obtained from the Cu surface after electropolishing and anodic polarization in the LiClO_4/PC solution at 0.1 mA cm^{-2} for 300 s are shown in Figs. 5 and 6, respectively. Peaks in the left- and right-hand side of spectra in the spectra are ascribed to electrons situated in $\text{Cu}(2p_{3/2})$ and $\text{O}(1s)$ energy levels, respectively. The number in the figure expresses the accumulated time (second) for etching of the sample surface by Ar^+ ion. As for the electropolished specimen, a single peak was observed near 933 eV, as seen in the left spectra of Fig. 5. This peak indicated existence of the Cu^0 and/or Cu^+ species. In general, it is difficult to distinguish the peaks attributed to both species owing to the considerably small difference in the energy level between them. Therefore, the valence state of the copper element is

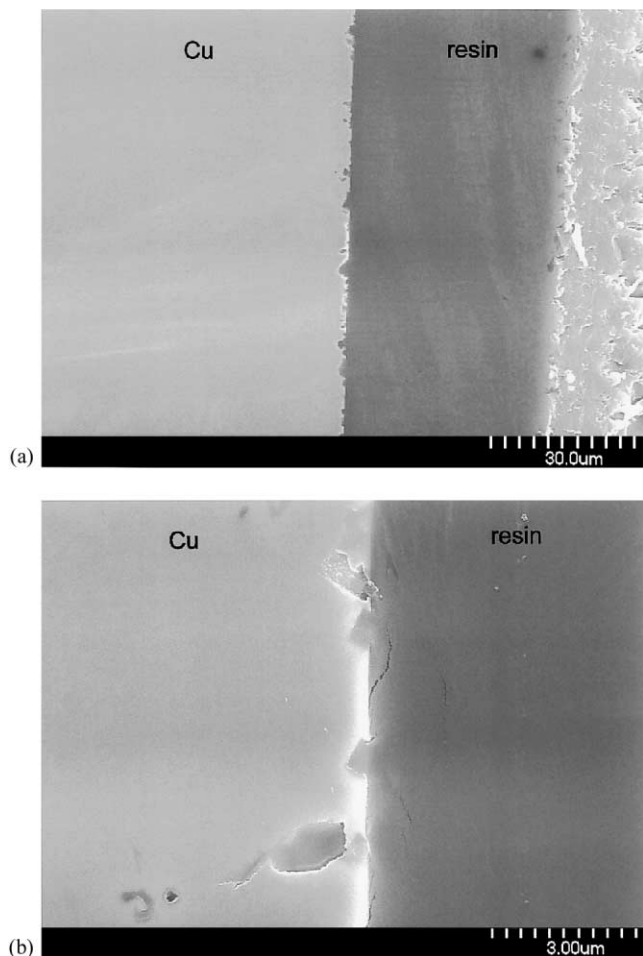


Fig. 4. SEM images of cross-section of Cu after polarization in LiClO_4/PC at 1.0 mA cm^{-2} for 300 s: (a) $1000\times$; (b) $10,000\times$.

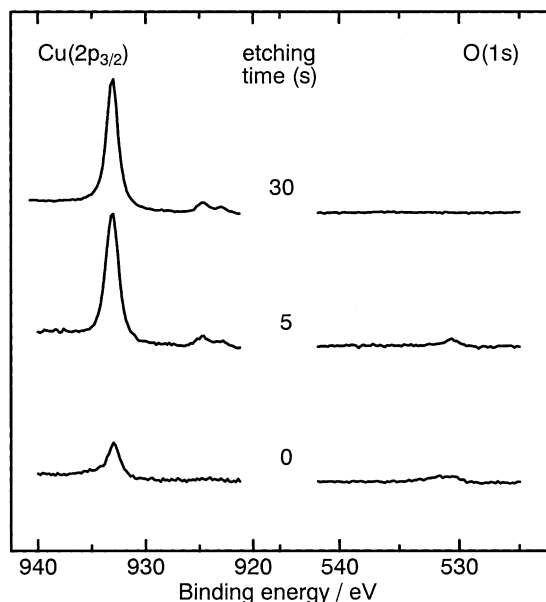


Fig. 5. XPS spectra of $\text{Cu}(2p_{3/2})$ and $\text{O}(1s)$ for electropolished Cu.

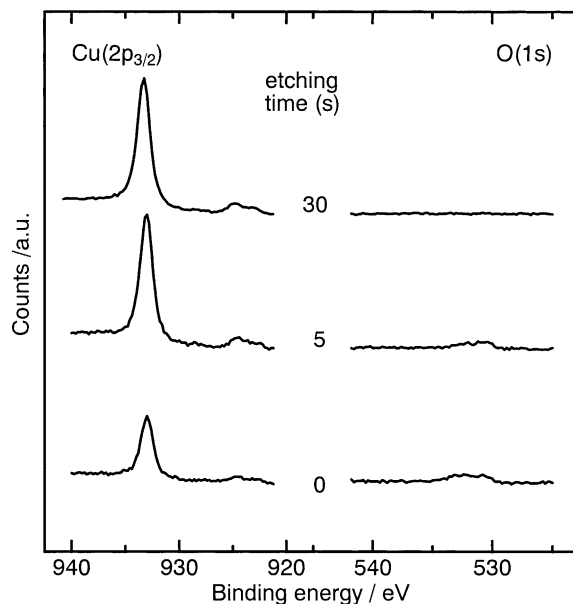
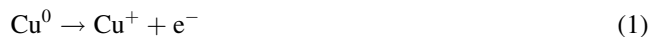


Fig. 6. XPS spectra of $\text{Cu}(2p_{3/2})$ and $\text{O}(1s)$ for Cu after polarization in LiClO_4/PC at 1.0 mA cm^{-2} for 300 s.

estimated from the energy level of another element such as oxygen. In this case, a weak and broad peak could be observed by etching within 5 s while it disappeared by etching more than 30 s. These results showed that the electropolished Cu substrate was covered with a considerably thin air-formed oxide layer. The anodically polarized specimen had a similar tendency of changes in spectra with the etching time, as seen in Fig. 6. In addition, no chlorine (Cl) element was detected by XPS measurement. Accordingly, the oxide film over the surface of Cu metal was significantly thin and formation of an additional oxidized product did not occur on the surface. This deduction was consistent with the result from the SEM observation (see Fig. 3).

Fig. 7 shows variations in resonance frequency and weight of the Cu electrode upon galvanostatically anodic polarization in the LiClO_4/PC solution, as drawn by solid lines. According to the Sauerbrey equation [23], the variation in weight was obtained by converting that in frequency obtained by the QCM measurement. The weight loss corresponds to removal of the substance from the electrode. In this case, electrochemical oxidation changed a metallic copper on the quartz disc into a copper cation in the electrolyte. Dashed lines show the values calculated by assuming that metallic copper (Cu^0) changes into cuprous (Cu^+) or cupric (Cu^{2+}) ion together with electron transfer, as follows:



Up to about 40 s, a decrement of the electrode in weight was close to the calculated value according to Eq. (1) while a

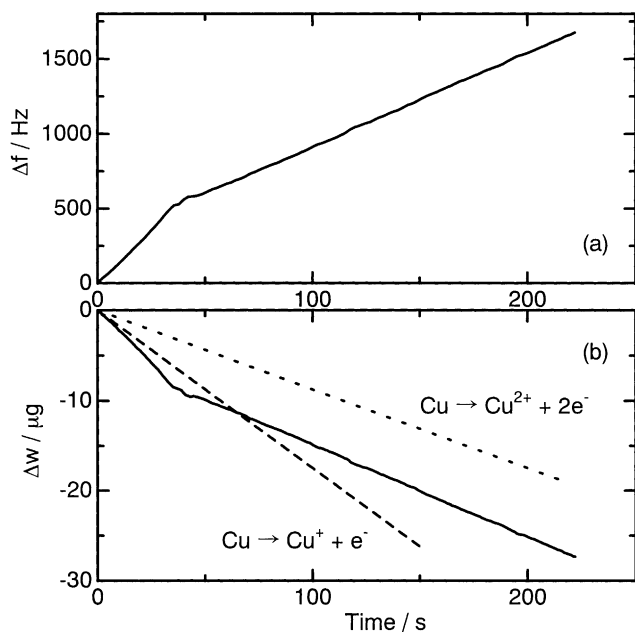


Fig. 7. Variations of Cu in (a) resonance frequency, Δf , and (b) weight, Δw , during polarization in LiClO_4/PC at 0.2 mA cm^{-2} (solid line: observed; dashed lines: calculated values).

gradual increase in electrode potential was observed. In general, Cu^+ is more likely than Cu^{2+} in a non-aqueous environment [24]. Therefore, Eq. (1) was reasonable to describe the reaction in an early stage of the galvanostatic polarization. The decrement of the electrode in weight became gradually larger than the calculated value. This phenomenon was explained by the viscosity of the electrolyte in touch with the electrode surface because the viscosity was changeable with increase of the Cu^+ ion formed by anodic polarization.

Over 40 s, the slope of the decreasing line became lower, indicating that the loss rate of copper from the electrode decreased. No abrupt change in electrode potential near 40 s corresponded to no change in reaction mechanism from Eqs. (1) to (2). Consecutively, the electrode potential kept almost constant around 3.5 V, which was consistent with the rising potential in the polarization curve (see Fig. 1). The SEM and XPS results showed no formation of oxide and progress of corrosion in this region. Accordingly, the bending of the decreasing line was caused by decomposition of the electrolyte on the electrode in competition with oxidative dissolution of the Cu substrate according to Eq. (1). Furthermore, the Faradaic efficiency of the reaction of oxidative dissolution was estimated to be 62%. This resulted from dividing the calculated value (-0.181 for Eq. (1)) into the observed one (-0.112) with respect to the slope of the straight line.

As for the electrode potential during polarization, EQCM took larger time to reach the steady value, compared to the polarization measurement of the electropolished specimen. The difference between them depended on the surface

state of the electrode. The electrode for EQCM had a considerably rough surface, which was formed by aggregation of small particles because it was prepared by evaporation of the Cu metal on the quartz crystal disc. Therefore, the EQCM electrode had a larger actual surface area with more defects and so oxidative dissolution was more feasible to take place on the Cu substrate, compared to the electropolished electrode.

4. Conclusion

Anodic polarization of copper in propylene carbonate revealed that oxidative dissolution of the metallic copper took place in competition with decomposition of the electrolyte. The oxidized copper existed as a cuprous ion (Cu^+). The reaction process was classified into a general corrosion caused by an activated dissolution of copper. This process left pits with the characteristic shape on the surface of the copper substrate. The shape of the pit depended on the crystallographic orientation of the copper grain. In a practical use, however, the corrosion of copper would not be realized on discharging of the negative electrode of the battery because the upper limit of its potential is estimated to be 1.5 V at most.

References

- [1] B. Scrosati, *J. Electrochem. Soc.* 139 (1992) 10.
- [2] J.M. Tarascon, D. Guyomard, *Solid State Ionics* 69 (1994) 293.
- [3] K. Kanamura, S. Toriyama, S. Shiraishi, Z. Takehara, *J. Electrochem. Soc.* 142 (1995) 1383.
- [4] A.M. Christie, C.A. Vincent, *J. Appl. Electrochem.* 26 (1996) 255.
- [5] T. Ohzuku, M. Kitagawa, T. Hirai, *J. Electrochem. Soc.* 137 (1990) 769.
- [6] T. Ohzuku, A. Ueda, M. Nagayama, *J. Electrochem. Soc.* 140 (1993) 1862.
- [7] J.R. Dahn, E.W. Fuller, M. Obravac, U. von Sacken, *Solid State Ionics* 69 (1994) 265.
- [8] G.G. Amatucci, J.M. Tarascon, L.C. Klien, *Solid State Ionics* 83 (1996) 167.
- [9] M. Doyle, J. Newman, A.S. Gozdz, C.N. Schmutz, J.M. Tarascon, *J. Electrochem. Soc.* 143 (1996) 1890.
- [10] K.V. Rybalka, L.A. Beketaeva, *J. Power Sources* 42 (1993) 377.
- [11] L.J. Krause, W. Lamanna, J. Summerfield, M. Engle, G. Korba, R. Loch, R. Atanasoski, *J. Power Sources* 68 (1997) 320.
- [12] K.V. Rybalka, L.A. Beketaeva, *Russ. J. Electrochem.* 34 (1998) 1262.
- [13] J.W. Braithwaite, A. Gonzales, G. Nagasubramanian, S.J. Lucero, D.E. Peebles, J.A. Ohlhausen, W.R. Cieslak, *J. Electrochem. Soc.* 146 (1999) 448.
- [14] K. Wang, P.N. Ross Jr., *Surf. Sci.* 365 (1996) 753.
- [15] M. Morita, Y. Matsuda, *J. Power Sources* 60 (1996) 179.
- [16] M. Ue, F. Mizutani, S. Takeuchi, N. Sato, *J. Electrochem. Soc.* 144 (1997) 3743.
- [17] W.K. Behl, E.J. Plichta, *J. Power Sources* 72 (1998) 132.
- [18] H.S. Choe, B.G. Carroll, D.M. Pasquaiello, K.M. Abraham, *Chem. Mater.* 9 (1997) 369.

- [19] Y. Chen, T.M. Devine, J.W. Evans, O.R. Monteiro, I.G. Brown, *J. Electrochem. Soc.* 146 (1999) 1310.
- [20] E. Skou, R. Koksang, S.Y. de-Andersen, J. Thomas, in: C.F. Holmes, A.R. Landgrebe (Eds.), *Batteries for Portable Applications and Electric Vehicles*, PV 97-18, The Electrochemical Society Proceedings Series, Paris, 1997, p. 19.
- [21] P. Arona, R.E. White, M. Doyle, *J. Electrochem. Soc.* 145 (1998) 3647.
- [22] J.W. Braithwaite, A. Gonzales, G. Nagasubramanian, S.J. Lucero, D.E. Peebles, J.A. Ohlhausen, W.R. Cieslak, *J. Electrochem. Soc.* 146 (1999) 448.
- [23] G. Sauerbrey, *Z. Phys.* 155 (1959) 206.
- [24] IUPAC Chemical Data Series-NO. 22, *Stability Constants of Metal-Ion Complexes, Part B, Organic Ligands*, Compiled by D.D. Perrin, Pergamon Press, New York, 1979.