

Electrochemical and X-ray photoelectron spectroscopy studies of carbon black as an additive in Li batteries

M. Manickam, M. Takata^{*}

Department of Electrical Engineering, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-2188, Japan

Received 23 May 2002; accepted 11 June 2002

Abstract

The effect of carbon black (acetylene black) as a cathode additive in lithium batteries was studied using electrochemical and X-ray photoelectron spectroscopy (XPS) measurements. The characteristic discharge curves for various weight percent (wt.%) of carbon black were obtained. The optimum wt.% of carbon black as a compromise between the desire to have active material present and the necessity to have a conduction path through the pores of the electrodes was obtained. It is shown that the behavior of carbon exhibits porosity rather than electronic conductivity. XPS results show that the C 1s peak at 283 eV corresponding to acetylene black, decreases during discharge and increases during charge. These results suggest that porosity of the electrode decreases during discharge and increases during charge.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Conductive additive; Porosity; Carbon black; X-ray photoelectron spectroscopy (XPS); Battery

1. Introduction

Several researchers have extensively investigated lithium rechargeable batteries, and various kinds of materials have been developed for use as cathodes, anodes and electrolytes. Great efforts have been made to identify the lithium-insertion compound that can be used as a cathode for a secondary lithium battery. Among the known lithium-insertion compounds, the layered compounds such as LiCoO_2 [1], LiNiO_2 [2] and the manganese–spinel framework system LiMn_2O_4 [3] are used commercially as 4.0 V positive electrode materials in rechargeable lithium batteries. However, the cathode material must be suitable as a host compound into and from which the working Li^+ ion can be inserted and extracted as a guest species during the discharge/charge cycle. This limits the use of layered and spinel structures as a cathode material.

The removal of Li from the layered $\text{Li}_{1-x}\text{MO}_2$ oxides renders them unstable at larger x relative to the displacement of M cations to the Li layers [4].

On the other hand, the spinel framework has no degrees of freedom for opening the interstitial space of the closely packed oxide ion array in which Li^+ ions move, so the $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ cathode is limited to low-power applications [5]. Although the $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ system has a flat open circuit

voltage at 3 V versus lithium, which is attractive [6], structural changes associated with a cooperative Jahn–Teller deformation of the framework tend to reduce the capacity irreversibly on repeated cycling [7].

Therefore, there is a motivation to identify an alternative framework host. One that has been recently explored is a NASICON-type compound, which is a good ionic conductor. The basis of the motivation to investigate a transition metal phosphate as a cathode and Li metal as anode will be the subject of a future paper [8]. For cathodes, carbon black is used as an additive to improve electrical conductivity [9]. Lahaye et al. [10] reported the influence of carbon black on the electrical properties of a MnO_2 –carbon black mixture which shows high electrical conductivity, and has led to the widespread use of carbon black as an additive in batteries. Subsequent to this, Fischer and Wissler [11] showed that the electrical conductivity of graphite increases with a decrease in particle size. Much of the work dealing with carbon as an additive to enhance electrical conductivity can be found in [12–15]. These authors have studied carbon black as an additive to improve the conductivity of the cathode mixtures. The scope of the studies reported in [12–15] is limited to enhancing the conductivity of the cathode.

Accelerated testing of additives for zinc plates in nickel/zinc cells was demonstrated by Biegler et al. [16] who showed that acetylene black individually enhanced zinc utilization over deep discharge cycles. They did not report,

^{*} Corresponding author. Tel.: +81-258-47-9509; fax: +81-258-47-3604.
E-mail address: takata@vos.nagaokaut.ac.jp (M. Takata).

however, the optimum level of these additives and to what extent they improve the discharge/charge behavior under practical conditions. In the present work, the effect of carbon black (acetylene black) used as a cathode additive in order to improve the battery capacity was studied by electrochemical and X-ray photoelectron spectroscopy (XPS) measurements. Besides screening additives Biegler et al. [16] discussed the mechanism of capacity loss was a decrease in the porosity of active material. Therefore, we investigated the role of porosity using various carbon content additives in cathode mixtures. Although the porosity measurements are not made in our study, based on Biegler et al.'s work, we assumed that the presence of pores in the active material with acetylene black as an additive allows the lithium ions to deeply penetrate into the electrode. It is plausible to assume that the large surface area of the electrode can be obtained as a result of the high porosity of the active material. Hence, by having a large real-surface area, a greater area is available for lithium intercalation into the electrode and the battery capacity is enhanced.

Here, we show that the added acetylene black significantly enhances the utilization of active material initially, but increasing carbon black contents result in a decrease in the total battery capacity. Our work suggests that the amount of porosity, not the presence of pores or cathode electrical conductivity, in the active material was the main origin of enhanced battery capacity.

2. Experimental

The active materials employed during electrode preparation were Li metal for the anode and transition metal phosphate, $\text{Cr}_{0.5}\text{Nb}_{1.5}(\text{PO}_4)_3$, for the cathode. The cathode was fabricated on a weight basis of 90–40% transition metal phosphate (active material), 10% PVDF (Aldrich) as binder and 0–50% acetylene black (Denka black). Hereafter, acetylene black will be referred to as A-black. The mixture was ground and then pressed into a disk shape with a diameter of 10 mm at 78 MPa. All disks (cathode) were mixed with binder, without which disks could not be handled. Each disk was 1 mm thick and weighed approximately 60 mg. The disks were dried at 80 °C for 30 min. An electrochemical testing cell was constructed with the disk as the cathode, lithium foil as the anode and filter paper as the separator. The electrolyte was 1 M LiClO_4 in EC/PC, 3:1 (v/v) (EC: ethylene carbonate, PC: propylene carbonate) (Tomiya). The cell performance was evaluated galvanostatically at a current density of 0.25 mA/cm² with the aid of charge–discharge unit (Hokuto Denko HJ-201B). The cells were first discharged and then charged at a constant current density between the potential limits of 1.5 V for discharge and 3.2 V for charge. All electrochemical measurements were carried out in a glove box filled with argon at room temperature. XPS (JEOL, JPS-9000 SX) using Mg K α radiation was used to analyze the chemical binding energy of the sample.

3. Results and discussion

The effect of A-black as the additive was investigated with various weight percent (wt.%) of A-black added to the cathode, as described in Section 2, while keeping other parameters constant for all cells tested. In Fig. 1, we compare the performance of electrodes with 0, 5, 10, 15, 20, 30, 40 and 50 wt.% A-black using the first discharge curve. The data represent discharge capacities that were calculated according to the weight of the active material. The shape of the discharge curves, irrespective of the wt.% (<0 wt.%), is characterized by an immediate sharp drop in voltage to 2.5 V followed by a gradual downward-sloping potential profile over a long period of time. Then, again, a sharp drop occurs at 2 V followed by a gradual change in voltage as a function of time until the cut-off voltage at 1.5 V.

It can be seen from Fig. 1 that the lowest material utilization is found in the electrode that does not contain any A-black. The capacity exhibited by such an electrode quickly drops to 1.5 V, which leads to 0 mAh/g. With 5 wt.% additive, electrode capacity dramatically increased to 70 mAh/g. For the cells with 10 and 15 wt.% additive, electrode capacity increased to a maximum of 108 and 135 mAh/g, respectively, whereas for the cells with ≤ 20 wt.% additive, capacity starts to decrease. The capacity difference is negligible between the cells having 15 and 20 wt.% A-black, however, the utilization of the cathode material was found to be higher for the electrode with 15 wt.% additive. It is important to note that for 5, 10, 40 and 50 wt.% additive, the gradually downward-sloping potential profiles were slightly lower and there was a rapid decrease in the battery capacity.

It is interesting to note the data presented in Fig. 2 showing that the conductivity of the cathode with 2–5 wt.% additive is higher than that with 0 wt.% additive and increases steeply; this confirms that A-black additive enhances the conductivity. However, the conductivity decreases dramatically as the A-black content increases above 5 wt.%. The cathode having an A-black composition >10 wt.% has a slightly lower conductivity than transition metal phosphate. Hence, the benefit of A-black on material utilization is not related to the electronic conductivity of the electrodes as described by other workers [12–15]. It is possible to assume that the improvement in capacity is due to the large surface area of the electrode, which means that pores are formed as a result of the use of A-black as an additive [16].

The material utilization depends strongly on the initial porosity and with discharge; the pore size decreases, thus limiting the transport of electrolytes to the interior of the pores [17]. Hence, a small amount of additive (5 wt.%) results in a small pore size which plays an important role in limiting the discharge capacity to 70 mAh/g, as shown in Fig. 3. Furthermore, this suggests that the higher the carbon content, the greater the area available (larger pore size) for

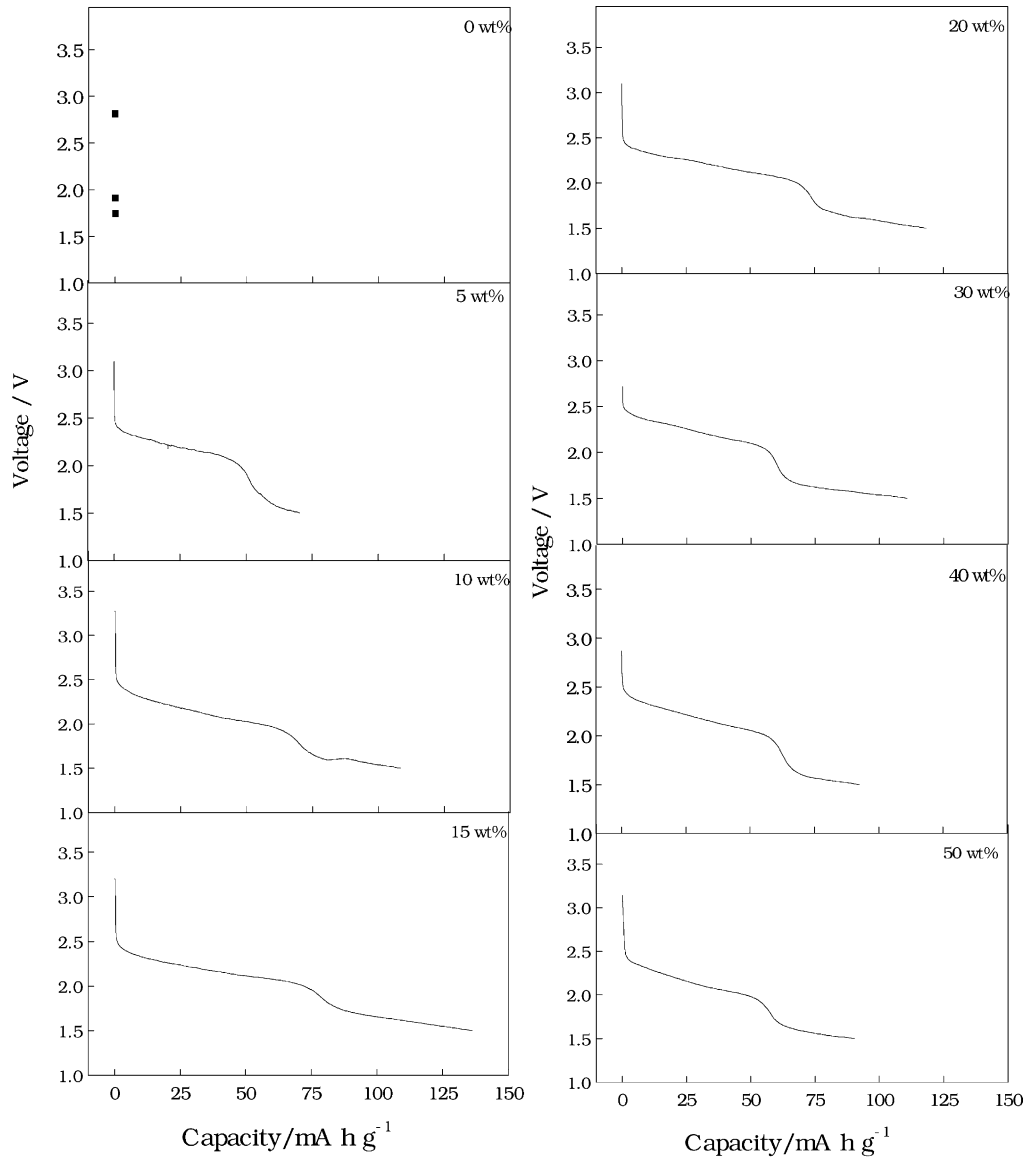


Fig. 1. The effect of acetylene black additive on the cathode discharge profile. The cathodes are composed of $\text{Cr}_{0.5}\text{Nb}_{1.5}(\text{PO}_4)_3$, PVDF, and acetylene black (weight percent is indicated in the profiles).

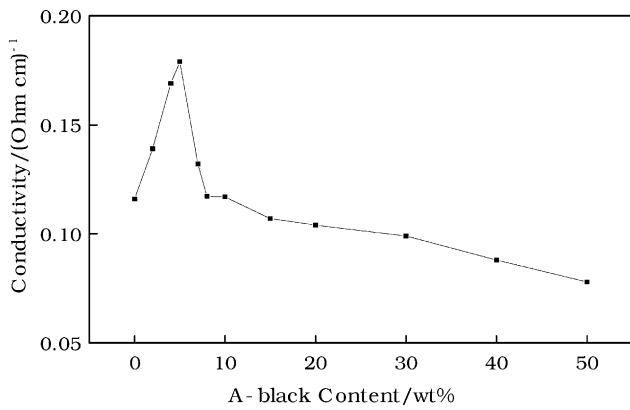


Fig. 2. Conductivity versus acetylene black content in the cathode containing $\text{Cr}_{0.5}\text{Nb}_{1.5}(\text{PO}_4)_3$ as active material, PVDF as binder (fixed) and acetylene black at various content.

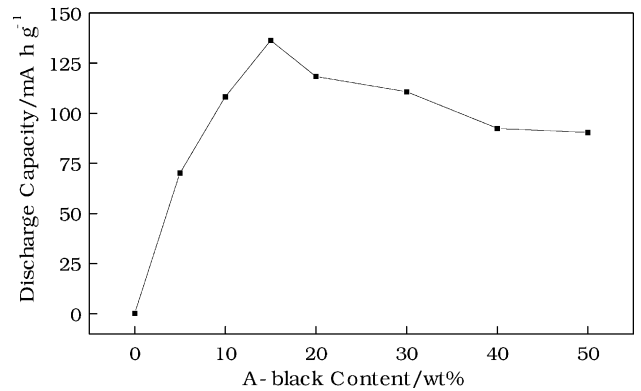


Fig. 3. Battery capacity behavior at various acetylene black contents in the cathode.

lithium insertion, and hence higher battery capacity could be obtained, confirmed the results of Biegler et al. [16]. Contrary to this, a cathode composition with more than 15 wt.% A-black results in a decrease in total battery capacity (>135 mAh/g), as shown in Fig. 3. This may be due to an intercalation reaction occurring further inside the pore that causes a loss of electrical potential in addition to slow diffusion. Thus, pores waste electrical energy, as well as help to increase the amount available per unit area. It is worth noting here that only a small part of any pore is active and there is a greater loss in beneficial capacity deeper into a pore at higher A-black contents.

Hence, the optimum weight percent as a compromise between the desire to have active material present and the amount of A-black necessary to have a conduction path through the pores of the electrodes was determined to be between 10 and 20 wt.% for this material. Among 10, 15 and 20 wt.% A-black, 15 wt.% appears to enable a good reversibility, as shown in Fig. 4 which shows the discharge–charge curves at the first cycle for the $\text{LiCr}_{0.5}\text{Nb}_{1.5}(\text{PO}_4)_3$ cells at a current density of 0.25 mA/cm^2 for different A-black contents in the cathode. The large voltage difference between discharge and midcharge curves shows that strong

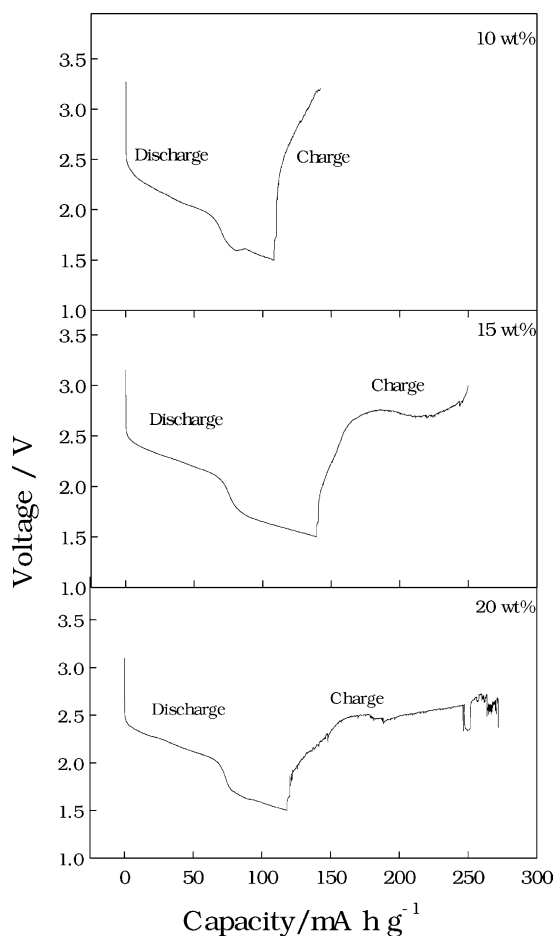


Fig. 4. First discharge/charge profiles of the cathode with acetylene black contents indicated in the profiles.

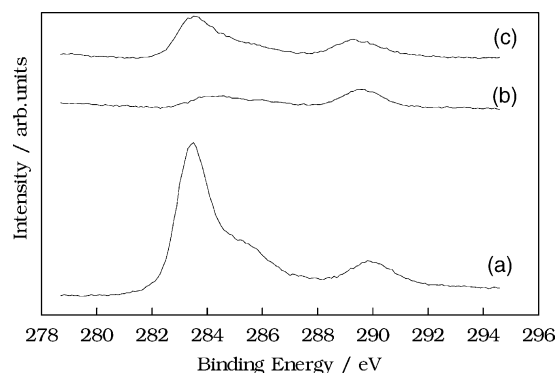


Fig. 5. XPS spectra of C 1s for the electrode (a) before cycling, (b) after first discharge (Li inserted), and (c) subsequent charge (Li extracted).

polarization occurs. This is due to low electronic conductivity [18]. For the electrode with 10 wt.% A-black, during the subsequent first charge, irreversible capacity loss is high (between 65 and 70%). This may be due to lithium trapped in the internal porosity. With 15 wt.% A-black, the irreversible capacity loss is limited (between 15 and 20%); this makes cyclability feasible for rechargeable lithium batteries. In contrast, 20 wt.% A-black results in an incomplete charge process and the same cut-off voltage cannot be attained. It is not fully understood why the charge process was not completed.

After the cells had been cycled at a current density of 0.25 mA/cm^2 , electrodes with 15 wt.% A-black were studied by XPS. For comparison, XPS of the sample before cycling was also performed. Fig. 5 shows the carbon spectra. The 1s spectrum of carbon in Fig. 5a has two different peaks, one at 290 eV, which can be assigned to Li_2CO_3 , and another at 283 eV, which is typical of A-black [19,20]. The intensity of the carbonate peak at 290 eV in Fig. 5b and c did not change significantly after the discharge and charge cycle. In contrast, the peak corresponding to A-black, Fig. 5b, decreased dramatically for discharge and then increased, for charge, Fig. 5c. It is assumed that as discharge continues, the actual thickness of the lithium electrode will gradually decrease due to anodic oxidation according to



Lithium ions travel through a separator and arrive at the pores in the cathode. At the end of discharge, most of the lithium ions will be migrated to the cathode and the volume originally occupied by the lithium will be replaced by the separator and the cathode (pores filled with Li^+). Therefore, the porosity of the cathode decreases during discharge and returns to its original value during charge. This assumption is consistent with the experimental results that the intensity of the C 1s spectra at 283 eV decreases dramatically after discharge and increases after charge but not to its original value. Therefore, these results suggest that acetylene black was utilized in the formation of porosity.

4. Conclusions

Acetylene black is commonly used as a conductive additive in lithium batteries. However, conductive additives are not passive materials and result in adverse side effects unless their role is widely studied. The role of A-black as an additive in lithium batteries is to provide porosity rather than electronic conductivity based on Biegler et al.'s discussion of porosity and our obtained discharge behavior of batteries with various weight percent of carbon and on the C 1s XPS spectrum.

The factors governing the capacity of the $\text{LiCr}_{0.5}\text{-Nb}_{1.5}(\text{PO}_4)_3$ cell were the optimum amount of A-black present in the cathode, and the pore size rather than that, the pores would increase the penetration depth, and hence the capacity, whereas their absence would decrease it as described by Biegler et al. [16]. The higher capacities shown with respect to carbon content are not due to higher electronic conductivity; rather, those advantages appear to be due to the amount of porosity in the cathode active material. With 5 wt.% carbon content, small pore size played a vital role in limiting the discharge capacity to 70 mAh/g; whereas composition >15 wt.% increased the penetration depth, resulting in a loss of electrical potential in addition to slow diffusion. Of the various carbon contents, 15 wt.% induced full electrode utilization, 135 mAh/g, and reversibility was attained in terms of discharge/charge profiles. Thus, the amount of porosity in the cathode active material with 15 wt.% A-black is most effective for the diffusion of Li^+ ions from the particle and leads to a high rechargeable capacity.

Based on XPS analysis, the intensity of the carbon peak corresponding to 283 eV decreased dramatically for discharge and then increased for charge. The XPS results on discharge and charge were interpreted using the porous assumption. This assumption is consistent with the XPS results of the intensity of C 1s spectra. Therefore, A-black has been utilized in the formation of porosity. However, further work is needed to identify to what extent they improve the cycle life of cells under practical conditions.

Acknowledgements

One of the authors (Manickam) wishes to acknowledge the financial support, in the form of an award of Monbusho fellowship by Ministry of Education, Science, Sports and Culture of Japan.

References

- [1] K. Mizushima, P.C. Jones, P.J. Wiseman, J.B. Goodenough, *Mat. Res. Bull.* 15 (1980) 783.
- [2] M.G.S.R. Thomas, W.I.F. David, J.B. Goodenough, *Mat. Res. Bull.* 20 (1985) 1137.
- [3] T. Ohzuku, M. Kitagawa, T. Hirai, *J. Electrochem. Soc.* 137 (1990) 769.
- [4] R.J. Gummow, M.M. Thackeray, *J. Electrochem. Soc.* 140 (1993) 3365.
- [5] M.M. Thackeray, J.O. Thomas, M.S. Whittingham, *MRS Bull.* 25 (2000) 39.
- [6] M.M. Thackeray, P.J. Johnson, L.A. de Piciotto, P.G. Bruce, J.B. Goodenough, *Mat. Res. Bull.* 19 (1984) 179.
- [7] M.M. Thackeray, A. de Kock, M.H. Roussow, D.C. Liles, R. Bittihn, D. Hoge, *J. Electrochem. Soc.* 139 (1992) 363.
- [8] M. Manickam, M. Takata, submitted for publication.
- [9] K. Kinoshita, *Carbon*, Wiley, New York, 1988, p. 403.
- [10] J. Lahaye, M.J. Wetterwald, J. Messiet, *J. Appl. Electrochem.* 14 (1984) 117.
- [11] F.G. Fischer, M. Wissler, *N. Mater. N. Process.* 3 (1985) 268.
- [12] K. Guerin, A. Fevrier-Bouvier, S. Flandrois, B. Simon, P. Biensan, *Electrochim. Acta* 45 (2000) 1607.
- [13] C.A. Frysz, X. Shui, D.D.L. Chung, *J. Power Sources* 58 (1996) 41.
- [14] S. Ahn, Y. Kim, K.J. Kim, T.H. Kim, H. Lee, M.H. Kim, *J. Power Sources* 81/82 (1999) 896.
- [15] J. Vondrak, I. Jakubec, J. Bludska, *J. Power Sources* 14 (1985) 141.
- [16] C. Biegler, R.L. Deutscher, S. Fletcher, S. Hua, R. Woods, *J. Electrochem. Soc.* 130 (1983) 2303.
- [17] W.G. Sunu, D.N. Bennion, *J. Electrochem. Soc.* 127 (1980) 2017.
- [18] C. Delmas, F. Cherkaoui, A. Nadiri, P. Hagenmuller, *Mat. Res. Bull.* 22 (1987) 631.
- [19] D. Aurbach, M.L. Daroux, P.W. Faguy, E. Yeager, *J. Electrochem. Soc.* 134 (1987) 1611.
- [20] K. Kanamura, H. Tamura, S. Shiraishi, Z. Takehara, *Electrochim. Acta* 40 (1995) 913.