

# Two-step addition of acetylene black to hydrated sodium manganese oxide: its effect on the performance of rapid discharge cathode

Mitsuhiro Hibino\*, Hirokazu Kawaoka, Haoshen Zhou, Itaru Honma

*Energy Electronics Institute, National Institute of Advanced Industrial Science and Technology (AIST),  
Tsukuba Central 2, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan*

Received 24 March 2003; received in revised form 21 April 2003; accepted 9 May 2003

## Abstract

Hydrated sodium manganese oxide (HSMO) was synthesized by reducing sodium permanganate with ethanol. The discharge and charge properties for mixtures of HSMO and acetylene black (AB) were investigated. AB was added twice, first while synthesizing HSMO and next while preparing the electrode. AB in synthesis resulted in the appearance of an additional redox reaction below 2 V versus Li/Li<sup>+</sup> and was effective in enlarging the discharge and charge capacity. On the other hand, AB added during electrode fabrication reduced resistance and improved cycle performance. In discharge–charge tests using 10 A g<sup>-1</sup> HSMO, 45 mAh g<sup>-1</sup> composite of specific capacity could be maintained after 10 cycles, if AB was added at levels (in weight ratio to HSMO) of 0.25 during synthesis and 0.75 in electrode fabrication, or 0.5 and 0.5, respectively. This current and capacity corresponded to a power density of 10 kW kg<sup>-1</sup> and an energy density of 90 Wh kg<sup>-1</sup>, assuming an operating voltage of 2.0 V.

© 2003 Elsevier B.V. All rights reserved.

*Keywords:* Sodium manganese oxide; Cathode material; Lithium battery; Rapid discharge; Composite material

## 1. Introduction

Recently, batteries that can discharge and charge rapidly are in high demand [1]. One strategy for developing such batteries is to improve existing energy devices: for example, enhancing the energy density of capacitors or the power density of lithium batteries. The electrodes of a capacitor must have a large surface area because the charge is accommodated on the surface of the material [2,3]. While enlargement of surface area is necessary to realize improved capacity, it is difficult to increase the surface area of the carbon materials currently used in electric double layer capacitors (EDLCs). In contrast, lithium intercalation provides intrinsically high capacity due to the use of the full volume of materials. Recently, Kudo et al. developed a composite electrode material that proved to be satisfactorily conductive and to have a large effective volume for lithium insertion: vanadium oxide gel was the active material coating acetylene black (AB) uniformly and thinly (ca. 50 nm) [4].

Especially in terms of cost, abundance, and non-toxicity, manganese oxides also constitute promising materials for the cathodes of lithium secondary batteries [5–7]. We fab-

ricated electrode materials consisting of manganese oxide and acetylene black in a sol solution based on a composite of vanadium oxide and AB; the specific capacity of the active material was 155 mAh g<sup>-1</sup> for rapid discharge under 10 A g<sup>-1</sup> [8]. This capacity corresponded to 78 mAh g<sup>-1</sup> and 5 A g<sup>-1</sup> on the basis of the weight of the composite containing both the active material and carbon. Assuming an operation voltage of 2.0 V, these values correspond to 10 kW kg<sup>-1</sup> of power density and 155 Wh kg<sup>-1</sup> of energy density. A battery made of such material may be expected to yield 2 kW kg<sup>-1</sup> and 31 Wh kg<sup>-1</sup>, respectively, assuming the factor of weight increase for other components to be about five. These values meet and even exceed the targeted ranges of 1.7–3.1 kW kg<sup>-1</sup> and 14–21 Wh kg<sup>-1</sup> for hybrid vehicle fast-response engines [9]. In the present study, we mixed manganese oxide with AB not only in synthesis but also in electrode fabrication and investigated the effects of each type of AB addition on discharge and charge performance.

## 2. Experimental

All samples were fabricated in essentially the same way as reported in [8]. We prepared two solutions: one was a

\* Corresponding author. Tel.: +81-29-861-3421; fax: +81-29-861-5829.  
E-mail address: [m.hibino@aist.go.jp](mailto:m.hibino@aist.go.jp) (M. Hibino).

dispersion liquid prepared by placing 1 ml of ethanol and the required amount of acetylene black (DENKA BLACK, Denki Kagaku Kogyo) into 40 ml of deionized water; the other was an aqueous solution of sodium permanganate ( $0.192 \text{ mol l}^{-1}$ , 60 ml), whose pH was lowered to about 1.0 by 1 ml of perchloric acid. Twenty-four hours after mixing those solutions, we filtered them and treated the filtrates thermally at  $120^\circ\text{C}$  for 3 h. For electrode preparation, AB and Teflon powders were added to the powder thus obtained. In our previous work, AB was not added during electrode fabrication [8]. The mixture was ground in a mortar agate and pressed on a nickel mesh (100 mesh). Electrochemical measurements were performed using a three-electrode beaker cell assembled in an inert gas system. For counter and reference electrodes, lithium metals were pressed on nickel mesh. We used  $1 \text{ M LiClO}_4/(\text{EC} + \text{DMC})$  (1:1 volume ratio) as the electrolyte.

### 3. Results and discussion

The samples consisted of hydrated sodium manganese oxide (HSMO) and AB. The empirical formula of HSMO

was previously determined to be  $\text{Na}_{0.05}\text{MnO}_{1.92}\cdot n\text{H}_2\text{O}$  from inductively-coupled plasma spectrometry and titration techniques for measuring the valence number of the manganese [8]. HSMO was thought to assume a random-stacked birnessite structure [8,10,11].

Fig. 1a–d show scanning electron micrographs for (a) AB, (b) the sample synthesized without AB, (c) the sample in which AB was added during electrode fabrication in a 1:1 (w/w) ratio with HSMO and (d) the sample in which AB was added during the synthesis procedure in a 1:1 (w/w) ratio with HSMO. Though AB particles seen in Fig. 1a have a characteristic morphology, such particles were not observed in Fig. 1d. From TEM observations, HSMO was found not to cover AB particles [8]. Therefore, Fig. 1d suggests that the AB surface changed and might have been roughened by treatment with the permanganate ion, a strong oxidizer. It is known that the surface structure of carbons such as furnace black and acetylene black decays by oxidation with nitric acid and that surface atoms are often removed in the form of water-soluble oxygenated functional groups [12]. In contrast, two kinds of particles are observed in Fig. 1c. One is similar to that seen in Fig. 1a and the other to that in Fig. 1b. Thus, the sample to which AB was added during the

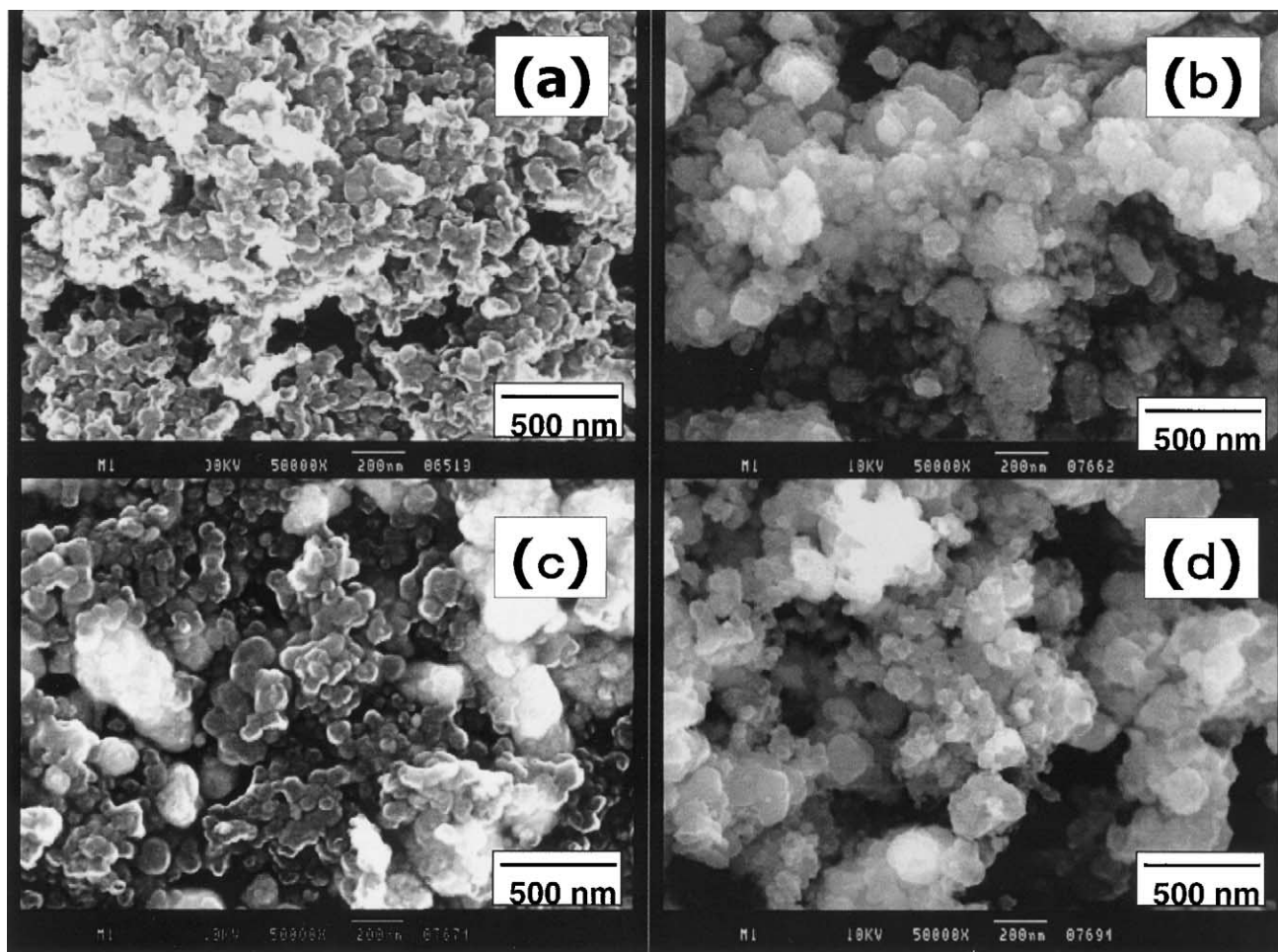


Fig. 1. SEM photographs for (a) AB, (b) HSMO, (c) HSMO and el-AB and (d) HSMO and s-AB.

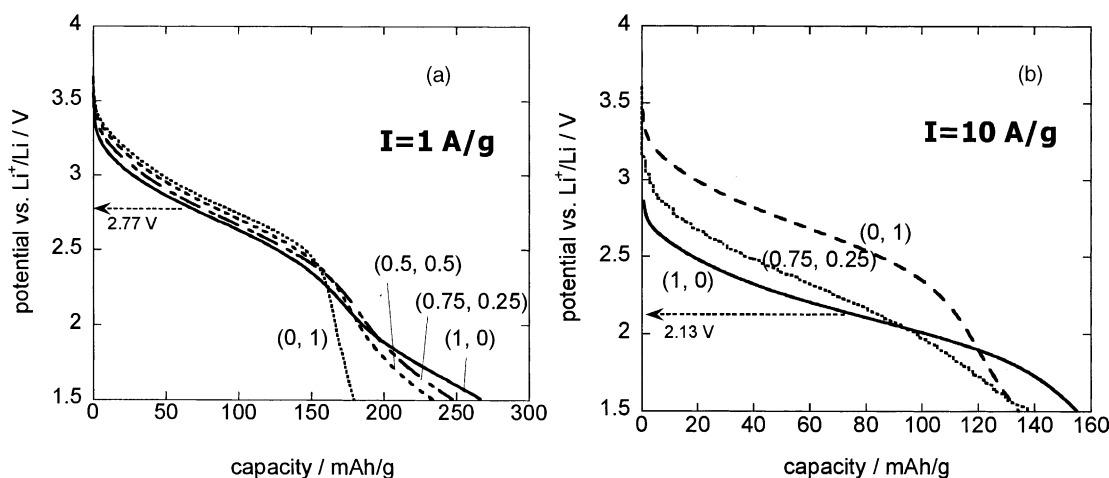


Fig. 2. Discharge curves for electrodes with additional AB (a)  $1 \text{ A g}^{-1}$  discharge and (b)  $10 \text{ A g}^{-1}$  discharge. Measures were based on weight ratios to HSMO. The weight ratio of AB to HSMO is described as (s-AB, el-AB).

procedure of electrode fabrication contained AB and HSMO particles unchanged from their original states. These results proved that AB occurs in different forms depending on the timing of its addition.

Fig. 2 shows the initial discharge profiles for samples containing HSMO and AB at equal weights. While the total AB remained constant, the relative amounts of AB added in synthesis and in electrode fabrication varied. Hereafter, AB added in synthesis and in electrode fabrication will be abbreviated to s-AB and el-AB, respectively. Each AB amount is expressed by a weight ratio to HSMO using parentheses, for example (0.25, 0.75). Calculation of the current density and specific capacity are based on the weight of HSMO. For  $1 \text{ A g}^{-1}$  of current density, all profiles show a similar behavior above 2.2 V versus  $\text{Li}/\text{Li}^+$  and a gradual slope around 2.8 V, where manganese reduces from  $\text{Mn(IV)}$  to  $\text{Mn(III)}$  [13]. Depending on the sample, the discharge curves above 2.0 V ranged between 170 and  $200 \text{ mAh g}^{-1}$ , which corresponds to 0.55–0.65 of the molar ratio of  $\text{Li}/\text{HSMO}$ . The average valence number of manganese at 2.0 V was estimated to be 3.22–3.14, a reduction from the initial valence number of 3.79 in  $\text{Na}_{0.05}\text{MnO}_{1.92}$ . Increasing s-AB enhanced the specific capacity, owing to the appearance of a new branch below 2 V. That might be attributed to the change in manganese valence state from  $\text{Mn(III)}$  to  $\text{Mn(II)}$  [13], though tetravalent manganese remained. For discharging under  $10 \text{ A g}^{-1}$ , the sample including larger s-AB exhibited lower potential but larger specific capacity. This tendency was enhanced by a large discharge current. For this reason, it was probably related closely to charge transfer resistance and resistance due to the lithium concentration gradient in particles of active material. In Fig. 2a and b, the potential for the sample with (s-AB, el-AB) = (1, 0) decreased from 2.77 to 2.13 V in response to an increase in current density from 1 to  $10 \text{ A g}^{-1}$ . If the electrochemical reaction observed below 2 V in discharges under  $1 \text{ A g}^{-1}$  had undergone an equal decline in discharge under  $10 \text{ A g}^{-1}$ , it would have disap-

peared and the increase in specific capacity by s-AB would not have been observed in discharges under  $10 \text{ A g}^{-1}$ . Instead, the specific capacity actually increased. Consequently, it can be inferred that reactions below 2 V have low resistance compared to those around 2.8 V. The sample with a larger el-AB retained a potential of about 2.8 V without appreciable decrease in potential for discharge under  $10 \text{ A g}^{-1}$ . We concluded that s-AB resulted in additional specific capacity below 2 V, that el-AB could reduce potential-drop due to resistance, which is its usual role as conducting additive, and that both s-AB and el-AB can enlarge specific capacity. We can obtain a suitable electrode material for particular operating conditions such as potential range or current density by finding the optimum mixing ratio of s-AB and el-AB.

The specific capacities of discharge between 4.3 and 1.5 V versus  $\text{Li}/\text{Li}^+$  are presented in Fig. 3. Discharge current density was  $10 \text{ A g}^{-1}$ . The current density for charge and discharge measurements is expressed on the basis of weight of

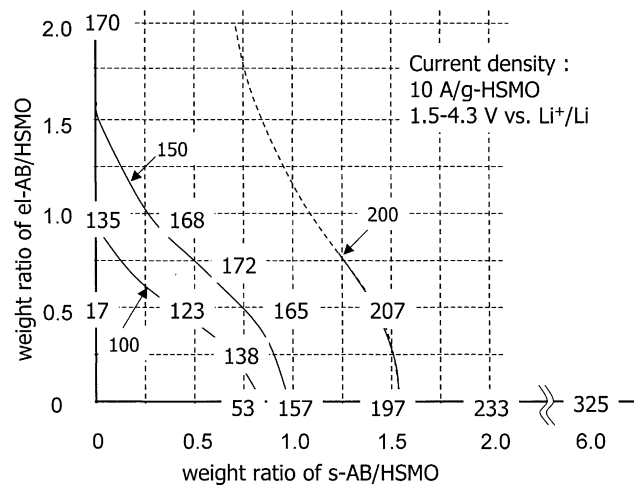


Fig. 3. Capacity mapping based on the weight of HSMO against the amount of s-AB and el-AB.

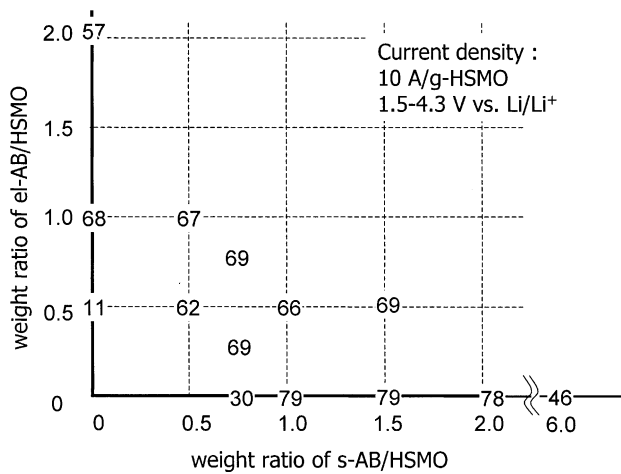


Fig. 4. Capacity mapping based on the weight of entire electrode (HSMO + AB) against the amount of s-AB and el-AB.

active material excluding AB unless otherwise noted. It was found that s-AB was more effective in increasing specific capacity than el-AB. The electrode in which s-AB was added at six times the weight of HSMO showed ca.  $325 \text{ mAh g}^{-1}$ . This is comparable to  $0.01 \text{ A g}^{-1}$  discharge of the electrode containing HSMO and s-AB at the same weight. It is natural that electrode performance for rapid discharge improves with greater AB additions, and that specific capacity based on total weight becomes more significant. Next, the capacity values in Fig. 3 were calculated on the basis of weight of composite and shown in Fig. 4. It is revealed that the addition of only s-AB in equal proportion to HSMO led to the largest capacity. At a discharge under  $1 \text{ A g}^{-1}$ , the addition of only s-AB at 75% of HSMO resulted in the largest capacity (data not shown). It seemed that el-AB was not necessary for high specific capacity though it reduced electric resistance.

Fig. 5a and b show capacity variation against cycle number. For  $10 \text{ A g}^{-1}$  of current density, AB was added at equal weight of HSMO; for  $1 \text{ A g}^{-1}$ , at 75% of HSMO weight. As described above, the electrodes showed the highest initial capacity for each current density when the AB was strictly s-AB. For some electrodes, the rate of capacity change became very slow and almost seemed to level off. The electrodes lacking el-AB deteriorated faster in discharge–charge at  $10 \text{ A g}^{-1}$  than at  $1 \text{ A g}^{-1}$ . Namely, the larger current tended to induce faster degradation. This phenomena can be explained as follows. If there exists in the electrode both highly conductive areas and poorly conductive ones, the electric current concentrates on the former area. Such current-intensive areas would quickly deteriorate. Electric non-homogeneity, therefore, should be avoided for favorable cycle performance, particularly at larger current discharges. Indeed, the improvement of cycle performance caused by el-AB was more marked for  $10 \text{ A g}^{-1}$  discharge than for  $1 \text{ A g}^{-1}$ . Consequently, el-AB was proven to be effective on cycle performance, especially for large current discharges.

The capacity after 10 cycles of discharge and charge between 1.5 and 4.3 V versus Li/Li<sup>+</sup> under  $10 \text{ A g}^{-1}$  are shown in Fig. 6. As in Fig. 4, the capacity was calculated on the bases of the weight of the entire electrode material, including HSMO, s-AB and el-AB. The highest capacity was found to be about  $45 \text{ mAh g}^{-1}$  for the samples whose (s-AB, el-AB) ratios to HSMO were (0.75, 0.25) or (0.5, 0.5). The corresponding power density and energy density were found from calculation to be  $10 \text{ kW kg}^{-1}$  and  $90 \text{ Wh kg}^{-1}$ , assuming an operating voltage of 2.0 V. Thus, electrodes including both s-AB and el-AB could be expected to retain a large energy density under high power use. Though the capacity degradation rate of these electrodes was very small, 10 cycles is too short period for testing practical cycle performance. Further research, especially on cycle performance, is necessary.

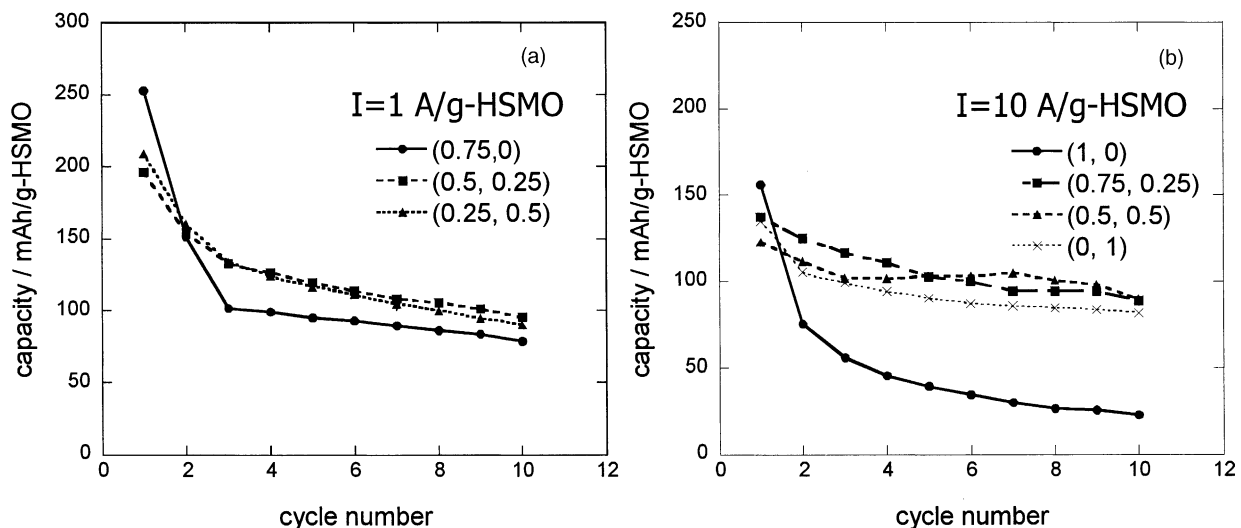


Fig. 5. Capacity variation during discharge–charge cycle under (a)  $1 \text{ A g}^{-1}$  and (b)  $10 \text{ A g}^{-1}$ . For  $1 \text{ A g}^{-1}$ , total AB was added in a ratio of 0.75 (w/w) to HSMO and for  $10 \text{ A g}^{-1}$ , in a 1:1 ratio.

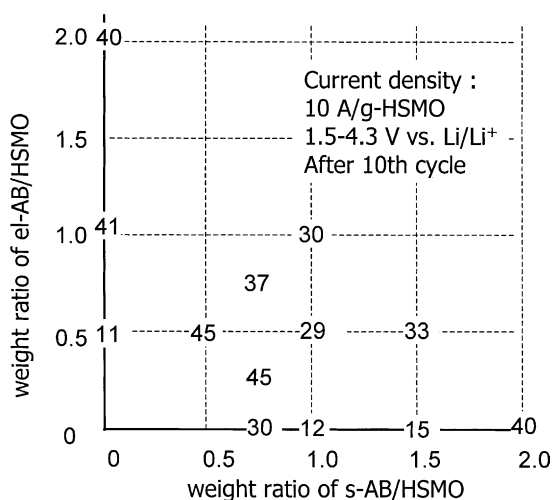


Fig. 6. Specific capacity after 10 cycles of discharge and charge on the basis of the weight of entire electrode (HSMO + AB) against amounts of s-AB and el-AB.

#### 4. Conclusions

In using hydrated sodium manganese oxide as the cathode material for lithium batteries, two-step AB addition is effective for preferable performance. AB was added during synthesis (s-AB) and during electrode preparation (el-AB). It was proven that the former increased specific capacity and that the latter lowered resistance and was especially valuable for preventing capacity deterioration caused by cycles. If electrodes were discharged and charged under  $10 \text{ A g}^{-1}$  HSMO of current density, the optimized mixing ratios to HSMO (w/w) were found to be 0.25 and 0.75 or 0.5 and 0.5

for s-AB and el-AB, respectively. Those electrodes showed  $45 \text{ mAh g}^{-1}$  of specific capacity. This performance corresponded to  $10 \text{ kW kg}^{-1}$  of power density and  $90 \text{ Wh kg}^{-1}$  of energy density, assuming an operating voltage of 2.0 V.

#### Acknowledgements

The present work was sponsored by the “Project of Fundamental Technology Development for Energy Conservation” of the New Energy and Industrial Technology Development Organization (NEDO).

#### References

- [1] B. Scrosati, *Nature* 373 (1995) 557.
- [2] I. Tanahashi, A. Yoshida, A. Nishino, *J. Electrochem. Soc.* 137 (1990) 3052.
- [3] J.P. Randin, E. Yeager, *J. Electroanal. Chem.* 36 (1972) 257.
- [4] T. Kudo, Y. Ikeda, T. Watanabe, M. Hibino, M. Miyayama, H. Abe, K. Kajita, *Solid State Ionics* 152–153 (2002) 833.
- [5] S. Atlung, T. Jacobsen, *Electrochim. Acta* 26 (1981) 1447.
- [6] M.M. Thackeray, W.I.F. David, P.G. Bruce, J.B. Goodenough, *Mater. Res. Bull.* 18 (1983) 461.
- [7] P.G. Bruce, *Chem. Commun.* 1817 (1997).
- [8] M. Hibino, H. Kawaoka, H.S. Zhou, I. Honma, *J. Electrochem. Soc.*, submitted for publication.
- [9] R.F. Nelson, *J. Power Sources* 91 (2001) 2.
- [10] D.S. Yang, M.K. Wang, *Chem. Mater.* 13 (2001) 2589.
- [11] S. Franger, S. Bach, J. Farcy, J.-P. Pereira Ramos, N. Baffier, *J. Power Sources* 109 (2002) 262.
- [12] K. Kamegawa, K. Nishikubo, M. Kodama, Y. Adachi, H. Yoshida, *Carbon* 40 (2002) 1447.
- [13] J.J. Xu, A.J. Kinser, B.B. Owens, W.H. Smyrl, *Electrochem. Solid State Lett.* 1 (1998) 1.