

Short communication

# Rechargeable solid-state battery using a proton-conducting composite as electrolyte

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Received 16 August 2001; accepted 5 January 2002

## Abstract

Proton-conducting composites of heteropolyacid hydrates (phosphotungstic acid, PTA and phosphomolybdic acid, PMA) with dispersoids such as insulating  $\text{Al}_2\text{O}_3$ ,  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$  and  $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 2\text{H}_2\text{O}$  are prepared for use as possible solid-state electrolytes in batteries. Bulk electrical conductivity as a function of composition is reported. Rechargeable solid-state proton batteries are fabricated and characterized. A cell with the configuration  $\text{Zn} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + \text{MH}_x | \text{PMA} + \text{APT} | \text{PbO}_2 + \text{V}_2\text{O}_5 + \text{C} + \text{E}$  gives an open circuit voltage of 1.5 V and can run for >850 h at a current drain of  $2.4 \mu\text{A cm}^{-2}$ . The cell can be recharged without much loss up to 18–20 cycles. © 2002 Published by Elsevier Science B.V.

*Keywords:* Battery; Composite; Proton-conducting; Rechargeable; Solid-state

## 1. Introduction

Recently, many attempts have been made to develop all solid-state batteries since this approach offers attractive features such as ease of fabrication, rugged construction, no liquid leaks, long shelf-life, miniaturization, safe, and a wide temperature range of operation. A number of batteries with  $\text{Li}^+$  or  $\text{Ag}^+$  ion conductors have been developed. Many studies have been reported on  $\text{Li}^+$ -based batteries because of the availability of good lithium ion conductors and a large electrochemical stability window [1,2], but high cost, difficulty in handling lithium electrodes and safety are some of the new problems. Recently, substantial progress has been made in the development of new proton conductors with high ionic conductivity. Hence, proton batteries can be considered as cost-effective alternatives [3,4] in spite of a smaller electrochemical stability window compared with  $\text{Li}^+$  batteries. Some of the well-known room temperature proton conductors are phosphotungstic acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ : PTA) and phosphomolybdic acid ( $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ : PMA) with high ionic conductivity [5]. The conductors tend to dehydrate under low humidity, however, and pelletization pressure leads to partial dehydration. In an attempt to overcome this problem, composites of heteropolyacid hydrates have been prepared by dispersing  $\text{Al}_2\text{O}_3$

or salt hydrates like  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$  and ammonium paratungstate ( $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 2\text{H}_2\text{O}$ : APT) since heterogeneous doping or the formation of dispersed phase composites has been found to be an efficient method for enhancing the ionic conductivity with good mechanical properties [6–8]. The present study involves the fabrication and characterization of a rechargeable solid-state battery using a suitable proton conducting ‘composite’ as electrolyte (PMA:APT composite). A hydrogen-storage material has been used for the anode, i.e. a light weight metal hydride (mischmetal-based aluminium nickelide  $\text{MmNi}_{4.5}\text{Al}_{0.5}$ ) developed in the authors’ laboratory [9]. The cathode material is an intercalating oxide such as  $\text{PbO}_2$  or  $\text{V}_2\text{O}_5$ .

## 2. Experimental

The materials employed were of analytical grade purity. The hydrogen storage material is mischmetal-based aluminium substituted pentanickelide ( $\text{MmNi}_{4.5}\text{Al}_{0.5}$ ), which was synthesized by ball milling technique [9]. The  $\text{MmNi}_{4.5}\text{Al}_{0.5}$  was exposed to hydrogen for 24 h to form a metal hydride.

Studies were made of electrical conductivity of the following composites: (i) PTA: $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ , (ii) PTA: $\text{Al}_2\text{O}_3$ , (iii) PMA: $\text{Al}_2\text{O}_3$ , (iv) PMA:APT, (v) PMA: $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ . The composites were prepared by simple physical grinding method and pellets of 8 mm diameter were made at a pressure of  $1 \times 10^3 \text{ kg cm}^{-2}$ . The electrical conductivity of the composites was evaluated by means of Solartron

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Frequency Response Analyzer (1250) with an electrochemical interface (1286) coupled to a computer. The frequency range of measurement was 65 Hz to 65 kHz. Graphite paste was applied to the electrodes for the conductivity measurements.

A solid-state proton battery was assembled by successively pressing the anode, the electrolyte and the cathode components in a pelletizing die. In the first step, the desired anode (i)  $\text{Zn} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  or (ii)  $\text{Zn} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + \text{MH}_x$  was obtained by pouring and then gently pressing in a die. The electrolyte powder (PMA + APT composite) was poured on to the compacted anode in the die and the assembly was again pressed gently. Next, the cathode mixture was poured into the die and pressed gently. The cathode mixture was ( $\text{PbO}_2 + \text{V}_2\text{O}_5 + \text{C} + \text{E}$ ) in the ratio 8:2:1:0.5. The entire assembly was finally compacted at  $3 \times 10^3 \text{ kg cm}^{-2}$  to obtain button-type cell. The cell dimensions were: thickness = 0.5 cm and area =  $0.76 \text{ cm}^2$ .

Immediately after the fabrication of the cell, the open-circuit voltage was measured with a high impedance multimeter (Keithley, 2000). The cell was allowed to stabilize for 8–10 h, after which the voltage became constant. The cells were charged under different loads and the variation of current

and voltage was monitored as a function of time. For rechargeability studies, the cell was discharged up to 10–20% of the initial voltage, and was then recharged using a constant-current source. After charging, the cell was again discharged and the charge–discharge cycle was repeated many times.

### 3. Results and discussion

#### 3.1. Conductivity of composite electrolytes

The variation of conductivity as a function of composition for (i) PTA: $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$  and PTA: $\text{Al}_2\text{O}_3$ , and (ii) PMA: $\text{Al}_2\text{O}_3$  and PMA:APT is shown in Figs. 1 and 2, respectively. In the case of  $x\text{PTA} + (1-x)\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ , the conductivity reaches a maximum value of  $1.1 \times 10^{-2} \text{ S cm}^{-1}$  (R.H.  $\sim 65\%$ ) at  $x = 0.5$ , and then decreases with further addition of  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ . There exists a small maximum at  $x = 0.7$ . In the case of the  $x\text{PTA} + (1-x)\text{Al}_2\text{O}_3$  composite, two peaks are observed at  $x = 0.8$  and 0.6. The enhancement is small compared with

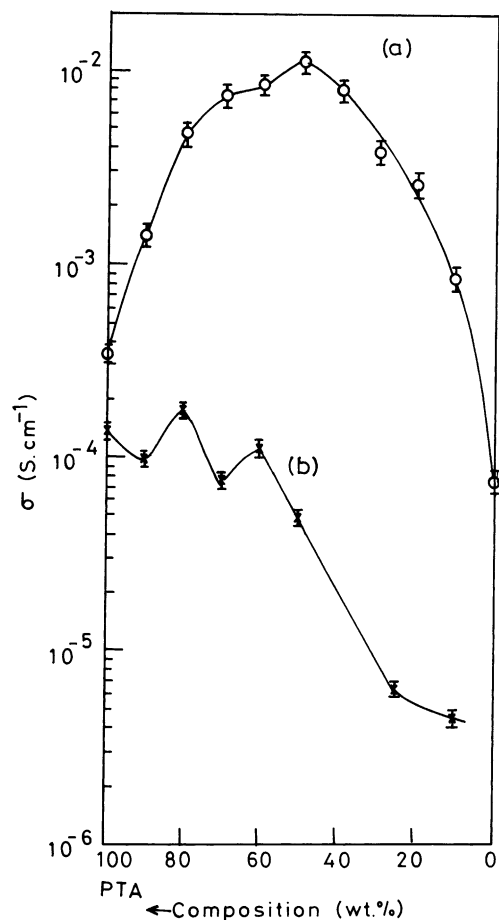


Fig. 1. Composition dependence of room temperature bulk conductivity of (a) PTA: $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$  (R.H.  $\sim 65\%$ ) and (b) PTA: $\text{Al}_2\text{O}_3$  (R.H.  $\sim 55\%$ ) composite systems.

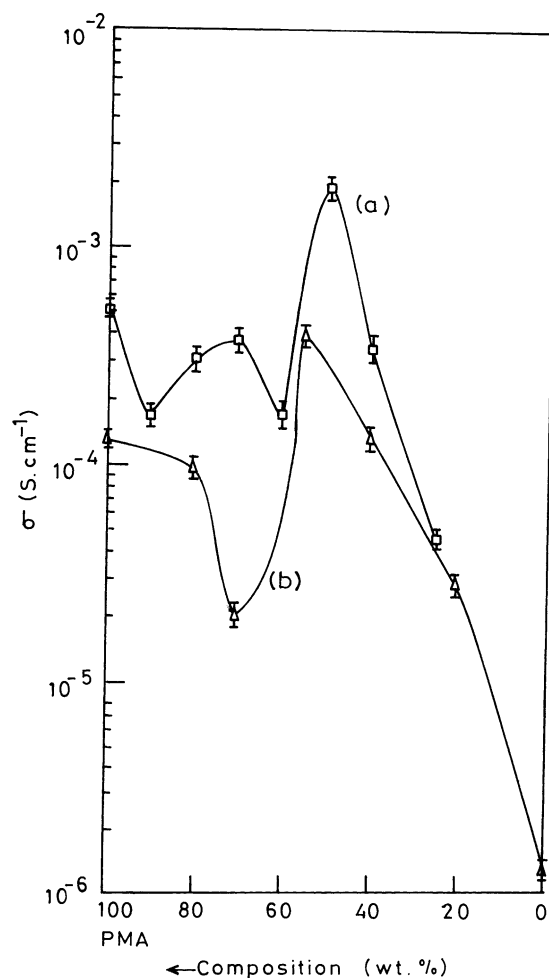


Fig. 2. Composition dependence of room temperature bulk conductivity of (a) PMA: $\text{Al}_2\text{O}_3$  (R.H.  $\sim 65\%$ ) and (b) PMA:APT (R.H.  $\sim 55\%$ ) composite systems.

that for the PTA: $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$  system which shows an increase in conductivity of approximately two-orders of magnitude. PMA: $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$  composite pellets are sticky and, hence, measurements cannot be made. For the  $x\text{PMA} + (1-x)\text{Al}_2\text{O}_3$  system (Fig. 2a), the conductivity–composition isotherm exhibits two maxima, a small one at  $x = 0.7$  and another  $x = 0.5$  with a maximum conductivity of  $1.8 \times 10^{-4} \text{ S cm}^{-1}$  (R.H.  $\sim 55\%$ ). Similarly, for the  $x\text{PMA} + (1-x)\text{APT}$  composite (Fig. 2b), the maximum conductivity is for  $x = 0.55$  ( $3.9 \times 10^{-4} \text{ S cm}^{-1}$  at 55% R.H.) and the second maxima (around  $x \sim 0.8$ ) is not so clear as in other cases.

The conductivity enhancement in dispersed phase systems with, for example,  $\text{Li}^+$ ,  $\text{Ag}^+$  or  $\text{Na}^+$  ion conductors has been well established [10–12]. Most of these studies report a single maxima in the conductivity–composition isotherm. The conductivity enhancement has been explained in terms of a ‘percolation threshold’ for the high conductivity interface paths at an optimum composition [11,12]. Proton-conducting systems have, however, to be viewed differently

from  $\text{Li}^+$ ,  $\text{Ag}^+$  or  $\text{Cu}^+$  systems because: (i) most proton conductors have more than one type of possible mobile species such as  $\text{H}^+(\text{H}_3\text{O}^+)$  and  $\text{OH}^-$ ; (ii) protonic species are highly reactive and, hence, may result in the formation of a new interface compound with the dispersoid. The existence of two maxima in the present ‘proton-conducting’ composites can be attributed to ‘two separate percolation thresholds’ for the two different types of mobile species  $\text{H}^+(\text{H}_3\text{O}^+)$  and  $\text{OH}^-$ . Another point to be noted is that the conductivity enhancement in the present proton-conducting composites as a result of dispersion of  $\text{Al}_2\text{O}_3$  in the heteropolyacids is less than that for corresponding  $\text{Li}^+$ ,  $\text{Ag}^+$  composites. This is because some of the mobile protonic species may bond with the amphoteric oxide  $\text{Al}_2\text{O}_3$  at the interface and result in the formation of new interface compound. Such a compound has been detected by means of XRD and DTA/TGA studies [13]. Such an interface reaction results in the loss of some of the mobile species and, hence, conductivity enhancement is less. Such a reaction is absent in PTA: $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$  and PMA:APT

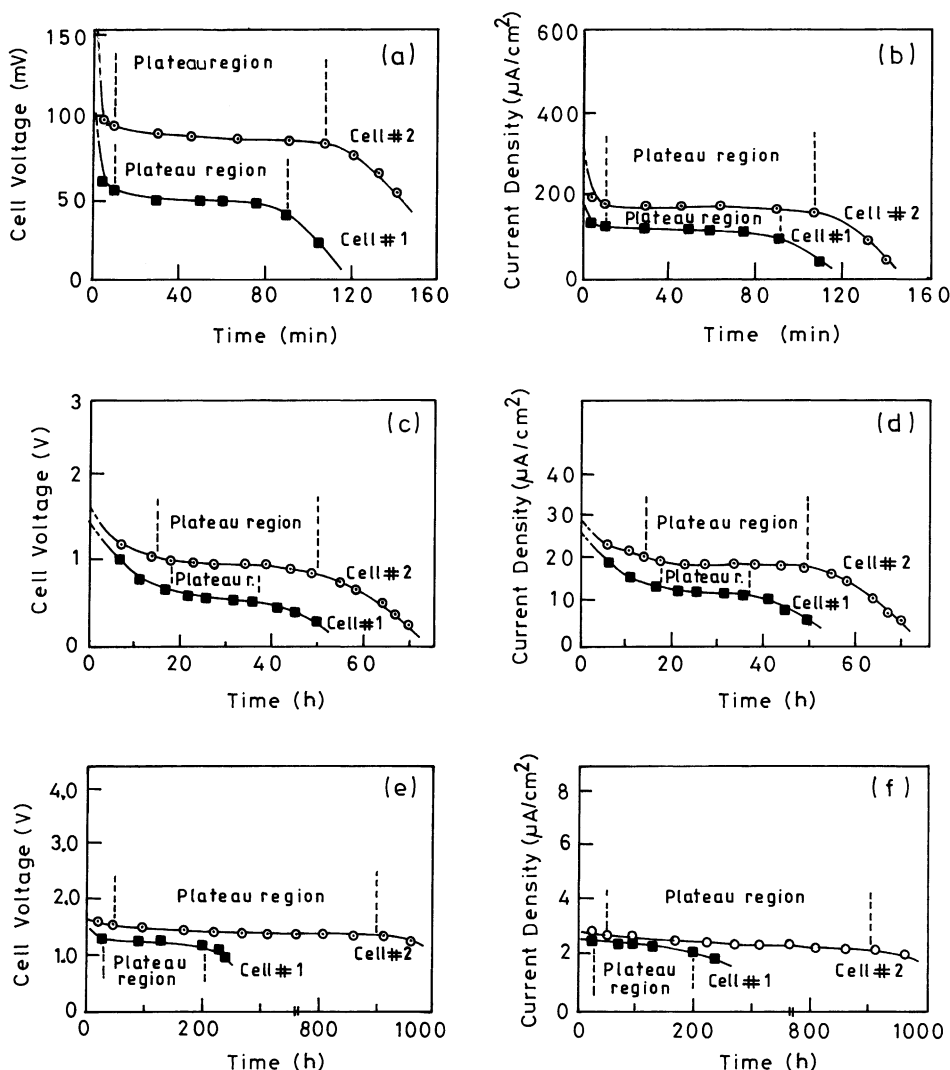


Fig. 3. Cell voltage and current density as a function of time for cells #1 and #2 at (a), (b) 1 k $\Omega$ ; (c), (d) 100 k $\Omega$ ; and (e), (f) 1 M $\Omega$  load.

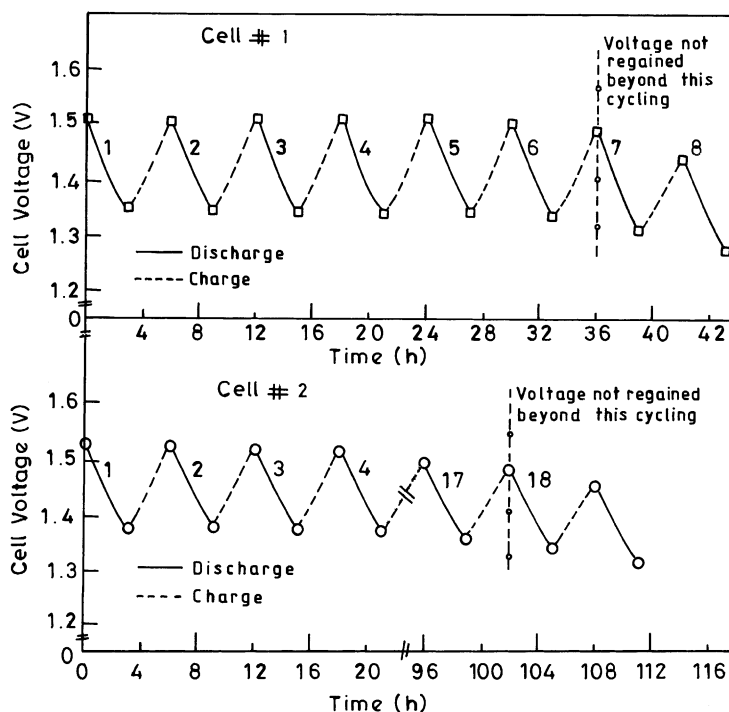


Fig. 4. Rechargeable studies of cells #1 and #2 showing variation of cell voltage with time during different discharge-charge cycles.

composites for which the conductivity enhancement is greater.

Earlier, we reported [14] studies on rechargeable solid-state proton battery using a PTA:Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·16H<sub>2</sub>O composite electrolyte. This proton-conducting composite (Fig. 1) has the best conductivity, but when used in the battery, the cell assembly was found to split under deep-discharge conditions. In the present work, we have fabricated and characterized a solid-state proton battery with a PMA + APT composite electrolyte which has the next best conductivity for the composites developed in our laboratories.

### 3.2. Discharge characteristics

The cells under study had the following configurations:

Cell #1: Zn + ZnSO<sub>4</sub>·7H<sub>2</sub>O|55%PMA + 45%APT|PbO<sub>2</sub> + V<sub>2</sub>O<sub>5</sub> + C + E

Cell #2: Zn + ZnSO<sub>4</sub>·7H<sub>2</sub>O + MH<sub>x</sub>|55%PMA + 45%APT|PbO<sub>2</sub> + V<sub>2</sub>O<sub>5</sub> + C + E

The discharge characteristics of cells #1 and #2 at 1, 100 kΩ and 1 MΩ loads are shown in Fig. 3a–c, respectively. When discharged under low load the voltage–current curve exhibits a rapid fall initially and then remains stable for a few hours (labeled as the plateau region in Fig. 3). Subsequently, the curve starts to decrease rapidly. When discharging at 100 kΩ and 1 MΩ, the period of stable performance increases. For the same electrolyte composition, the addition of metal hydride improves the period of stable performance due to the copious supply of H<sup>+</sup> ions available from the metal hydride. No swelling or splitting of the cell assembly is observed even under deep-discharge conditions in contrast

to that observed in with solid-state batteries based on PTA:Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·16H<sub>2</sub>O.

### 3.3. Rechargeability

The cathode used in the cells was a mixture of layered materials (PbO<sub>2</sub> + V<sub>2</sub>O<sub>5</sub>) which permits reversible intercalation–deintercalation of H<sup>+</sup> in its layers. Hence, multiple discharge–charge cycling of the battery becomes possible. To determine the rechargeability, the cells were discharged under a 50 kΩ load for a time *t*. The discharge was terminated after the cell voltage dropped by 10% of the initial value. The cells were recharged using a constant-current source. The typical rechargeability of cells #1 and #2 shown in Fig. 4. It has been found that cell #2 could be recharged for up to 18 cycles without significant loss in voltage, whereas the cell #1 could be recharged for only 7 cycles. The better rechargeability of cell #2 may be due to the presence of metal hydride in its anode compartment which maintains a continuous supply of hydrogen ions.

From the above studies, the important battery parameters have been evaluated for the cell #2, and are as follows:

|  |      |
|--|------|
| Cell weight (mg)                                     | 700  |
| Cell area (cm <sup>2</sup> )                         | 0.76 |
| Open-circuit voltage (V)                             | 1.5  |
| Short-circuit current (mA)                           | 1.1  |
| Specific power <sup>a</sup> (mW kg <sup>-1</sup> )   | 21   |
| Specific energy <sup>a</sup> (mWh kg <sup>-1</sup> ) | 735  |
| Discharge capacity <sup>a</sup> (mAh)                | 0.53 |

<sup>a</sup> Calculated for the stable plateau region.

#### 4. Conclusions

Rechargeable solid-state proton batteries have been fabricated using a PMA:APT composite electrolyte and an intercalating layered cathode. The addition of metal hydride in the anode compartment improves both the period of stable performance and the rechargeability as it ensures a continuous supply of H<sup>+</sup> ions. A cell with configuration Zn + ZnSO<sub>4</sub>·7H<sub>2</sub>O + MH<sub>x</sub>|55%PMA + 45%APT|PbO<sub>2</sub> + V<sub>2</sub>O<sub>5</sub> + C + E can be recharged for up to 18 cycles without much loss of voltage or capacity. It gives a current density of ~2.4 μA cm<sup>-2</sup> for >850 h.

#### Acknowledgements

Thanks are due to CSIR, New Delhi for Providing a Senior Research Fellowship to N. Lakshmi and an Emeritus Scientist project to S. Chandra.

#### References

- [1] S. Chandra (Ed.), *Superionic Solids—Principles and Applications*, North Holland, Amsterdam, 1981.
- [2] M.Z.A. Munshi (Ed.), *Handbook of Solid-State Batteries and Capacitors*, World Scientific, Singapore, 1995.
- [3] Ph. Colomban (Ed.), *Proton Conductors: Solids, Membranes and Gels—Materials and Devices*, Cambridge University Press, New York, 1992.
- [4] J. Guittou, B. Dongui, R. Mosdale, M. Forestier, *Solid State Ion.* 28–30 (1988) 847.
- [5] O. Nakamura, T. Kodama, I. Ogino, Y. Miyake, *Chem. Lett.* (1979) 17.
- [6] C.C. Liang, *J. Electrochem. Soc.* 120 (1973) 1289.
- [7] J. Maier, *J. Phys. Chem. Solids* 46 (1985) 309.
- [8] K. Shahi, J.B. Wagner Jr., *J. Solid-State Chem.* 42 (1982) 107.
- [9] A.Kr. Singh, A.K. Singh, O.N. Srivastava, *Int. J. Hydrogen energy* 18 (1993) 567.
- [10] J. Maier, *Prog. Solid-State Chem.* 23 (1995) 171.
- [11] A. Bunde, W. Dieterich, E. Roman, *Solid-State Ion.* 18/19 (1986) 147.
- [12] A. Bunde, *Solid-State Ion.* 75 (1995) 147.
- [13] N. Lakshmi, S. Chandra, *Phys. Stat. Soli. (a)* 186 (2001) 383.
- [14] K. Pandey, N. Lakshmi, S. Chandra, *J. Power Sources* 76 (1998) 116.