

Polymer Ni–MH battery based on PEO–PVA–KOH polymer electrolyte

Chun-Chen Yang*

Department of Chemical Engineering, Ming-Chi Institute of Technology, 84 Gungjuan Road, Taishan, Taipei Hsien, Taiwan, ROC

Received 24 August 2001; accepted 9 January 2002

Abstract

An alkaline polymer electrolyte film has been prepared by a solvent-casting method. Poly(vinyl alcohol), PVA is added to improve the ionic conductivity of the electrolyte. The ionic conductivity increases from 10^{-7} to 10^{-2} S cm^{-1} at room temperature when the weight percent ratio of poly(ethylene oxide), PEO to PVA is increased from 10:0 to 5:5. The activation energy of the ionic conductivity for the PEO–PVA–KOH polymer electrolyte is 3–8 kJ mol^{-1} . The properties of the electrolyte film are characterized by a wide variety of techniques and it is found that the film exhibits good mechanical stability and high ionic conductivity at room temperature. The application of such electrolyte films to nickel–metal–hydride (Ni–MH) batteries is examined and the electrochemical characteristics of a polymer Ni–MH battery are obtained. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Polymer electrolyte; Poly(ethylene oxide); Poly(vinyl alcohol); Ionic conductivity; Nickel–metal–hydride battery

1. Introduction

Solid polymer electrolytes (SPEs) have been studied extensively in recent years for application in many electrochemical devices, such as cellular phones, smart credit cards, and laptop computers [1]. A polymer complex consisting of polyethylene oxide (PEO), plasticizers and alkali metal salts was discovered by Wright et al. [2,3] and Armand et al. [4] as a solvent-free polymer electrolyte. Although a PEO-based SPE can form a dimensionally stable film, its ambient temperature conductivity is only in the range of 10^{-7} to 10^{-8} S cm^{-1} . This is too low for application in electrochemical devices. In order to enhance the conductivity, several approaches have been suggested. These have included polymer blends, polymers modified with plasticizers or mixtures of solvents, and gel electrolytes. The main objective of such studies has been to obtain films with a high fraction of amorphous phase as this exhibits a much higher conductivity than the crystalline phase.

Some of the research studies have focused on PEO-based electrolytes with lithium salts and organic solvents. The polymer lithium system appears to be the most widely studied due to its potential application in high-density batteries. In contrast, there are only few published reports

of alkaline solid polymer electrolytes based on the PEO–KOH system [5–8]. Alkaline SPEs can be applied in all-solid alkaline rechargeable batteries. In this work, we report the preparation and properties of an alkaline SPE based on the PEO–PVA–KOH–water polymer electrolyte (PVA: poly(vinyl alcohol)).

In general, a nickel–metal–hydride (Ni–MH) batteries shows better operational properties than nickel–cadmium batteries, namely; shows better higher specific energy, no contamination, and no memory effect. Portable devices, the main application of Ni–MH batteries demand high specific energy and specific power. Thus, the alkaline polymer Ni–MH battery appears to be a good candidate for future such applications. Lichtenberg and Kleinsorgen [9] studied the properties of Ni(OH)₂ electrodes with CoO and Co additives. Other workers [10–19] investigated the surface treatment for Ni(OH)₂ powder and its effects as an additive on Ni–MH battery performance. In this paper, the ionic conductivity of SPE films is measured by means of an ac impedance method. The electrochemical stability window is examined by cyclic voltammetry. The amorphous of SPE films is analyzed in terms of the glass transition temperature (T_g) measured by differential scanning calorimetry (DSC). Thermal stability is examined by thermal gravimetric analysis. A scanning electron microscope (SEM) is used to examine the surface morphology of the polymer electrolyte film. Finally, electrochemical characteristics of a polymer Ni–MH battery are investigated.

* Tel.: +88629089899; fax: +886229041914.

E-mail address: ccyang@ccsun.mit.edu.tw (C.-C. Yang).

2. Experimental

PEO (M_w 100,000, Aldrich), PVA (M_w 130,000, Aldrich), and KOH (Merck) were used as received. The alkaline solid polymer electrolyte films were prepared by a solvent-casting method. The appropriate weight ratios of PEO and PVA were dissolved in water with various amounts (wt.%) of KOH. The solution was stirred continuously until the mixture became a homogeneous viscous liquid. The resulting solution was poured on to a glass plate and weighed immediately. The excess water was evaporated off slowly. After evaporation, the glass plate and the film was weighed again. The film composition was determined from the mass balance. The thickness of the films was between 0.2 and 0.4 mm.

Conductivity measurements were made for the polymer electrolyte film by an ac two-terminal method. The sample films were sandwiched between SS316 stainless-steel, ion-blocking electrodes (surface area of each: 0.785 cm^2) in a spring-loaded glass holder. A thermocouple was kept close to the electrolyte film for temperature measurements. Cyclic voltammetry and ac impedance measurements were performed by means of an EG&G impedance spectrometer model 273A+1025 and a computer program EG&G model 398. The frequency range was 300 kHz to 0.10 Hz at an excitation signal of 5 mV. The impedance of the sample film was measured from 20 to 60 °C. Temperatures were maintained within ± 0.2 °C by performing experiments in a convection oven.

DSC thermal analysis was conducted with a Perkin Elmer Pyris 7 DSC system. Measurements were made by heating from -70 to 220 °C at a heating rate of 10 °C min^{-1} in a nitrogen atmosphere with about 5 to 10 mg of sample. TGA thermal analysis was carried out with a Perkin Elmer Pyris 7 TGA system. Measurements were made by heating from 30 to 600 °C, under nitrogen atmosphere at a heating rate of 10 °C min^{-1} with 5–10 mg of sample. The surface morphology and microstructure of the sample films were characterized with a S-2600H scanning electron microscope (Hitachi Co., Ltd.)

Pasted nickel electrodes were made of $\text{Ni}(\text{OH})_2$ powder, acetylene black, and PTFE binder. A $2 \text{ cm} \times 2 \text{ cm}$ sheet of nickel foam saved as the substrate, with a nickel wire spot-welded to the edge as a terminal. The $\text{Ni}(\text{OH})_2$ powder, acetylene black, CoO and PTFE binder were mixed together in the respective percent proportions of 70:15:10:5. The solid mixture was mixed with IPA solvent to form a paste. The paste was placed in the nickel-foam substrate dried at 100 °C for 1 h, and then pressed at 2 ton cm^{-2} . The $\text{Ni}(\text{OH})_2$ electrode was immersed in 30% KOH solution for 24 h in an open cell for testing.

The metal-hydride electrode was a commercial available AB_5 type alloy. The capacity of the electrode is limited by the $\text{Ni}(\text{OH})_2$ electrode. The activated $\text{Ni}(\text{OH})_2$ or MH electrode was used as a working electrode. The electrolyte was aqueous 30% KOH solution. A platinum screen and a

mercury oxide electrode ($\text{HgO}/\text{Hg}/6 \text{ M KOH}$) were used as a counter electrode and a reference electrode, respectively. The PEO–PVA–KOH polymer electrolyte was sandwiched between an activated $\text{Ni}(\text{OH})_2$ electrode and activated MH electrode for 24 h in a closed cell. Several alkaline polymer Ni–MH cells were charged for 7.5 h at C/5, kept for 30 min at open circuit, and then discharged at the C/5 rate to 0.8 V. Charge–discharge cycles were performed at room temperature with Maccor 2200 model equipment. The cycling experiments were carried out after the cell had reached a stable condition (usually, 4–5 cycles).

3. Results and discussion

The DSC curves of PEO–KOH and PEO–PVA–KOH systems are shown in Fig. 1. An endothermic peak is observed at 61 °C, which corresponds to the melting temperature of PEO, as shown in Table 1. It was found that the melting temperature, T_m , of PEO shifts towards a lower temperature when the PVA is added to the PEO-based polymer system. The change in T_m of PEO-based polymer indicates a change from a semi-crystalline to an amorphous phase. It is found that the polymer electrolyte converts completely to an amorphous state when the PVA ratio is above 50%, such as PEO:PVA = 5:5. The increase in conductivity with temperature due to a hopping mechanism between coordinate sites, and local structural relaxation and segmental motions of the polymer. The segmental motion occurs more readily in the amorphous polymer backbone. In general, a SPE polymer electrolyte requires a low T_g , which is one of the important factors. It is found that the PEO based polymer electrolyte on adding PVA has a higher T_g than PVA-free polymer. The T_g of the PEO-based polymer increases with increases in PVA content, which indicates a greater rigidity of the amorphous system due to the occurrence of ionic interactions.

The TGA curves for the PEO–PVA–KOH system are shown in Fig. 2. There is a weight loss of 97% at a temperature of 372 °C for the pure PEO polymer. A significant weight loss for PEO–PVA–KOH polymer electrolyte (i.e. PEO:PVA = 8:2) begins at temperature of 360 °C, and is 95.3% after 400 °C. Complete homogeneity of the polymer electrolyte is observed because the film shows degradation

Table 1
Conductivity and thermal properties of PEO–PVA–KOH polymer electrolyte

Property	PEO:PVA (10:0)	PEO:PVA (8:2)	PEO:PVA (5:5)	PEO:PVA (2:8)
σ (S cm^{-1}) at 25 °C	428×10^{-7}	7.43×10^{-6}	0.0577	0.0608
E_a (kJ mol^{-1})	20.15	13.40	7.62	2.33
$T_{g,\text{PEO}}$ (°C)	-62.01	-56.77	-50.08	–
$T_{m,\text{PEO}}$ (°C)	61.17	58.81	–	–

Note: $T_g = 62.69$ °C; $T_m = 61$ °C for PEO polymer; $T_g = 86.60$ °C; $T_m = 210$ °C for PVA polymer.

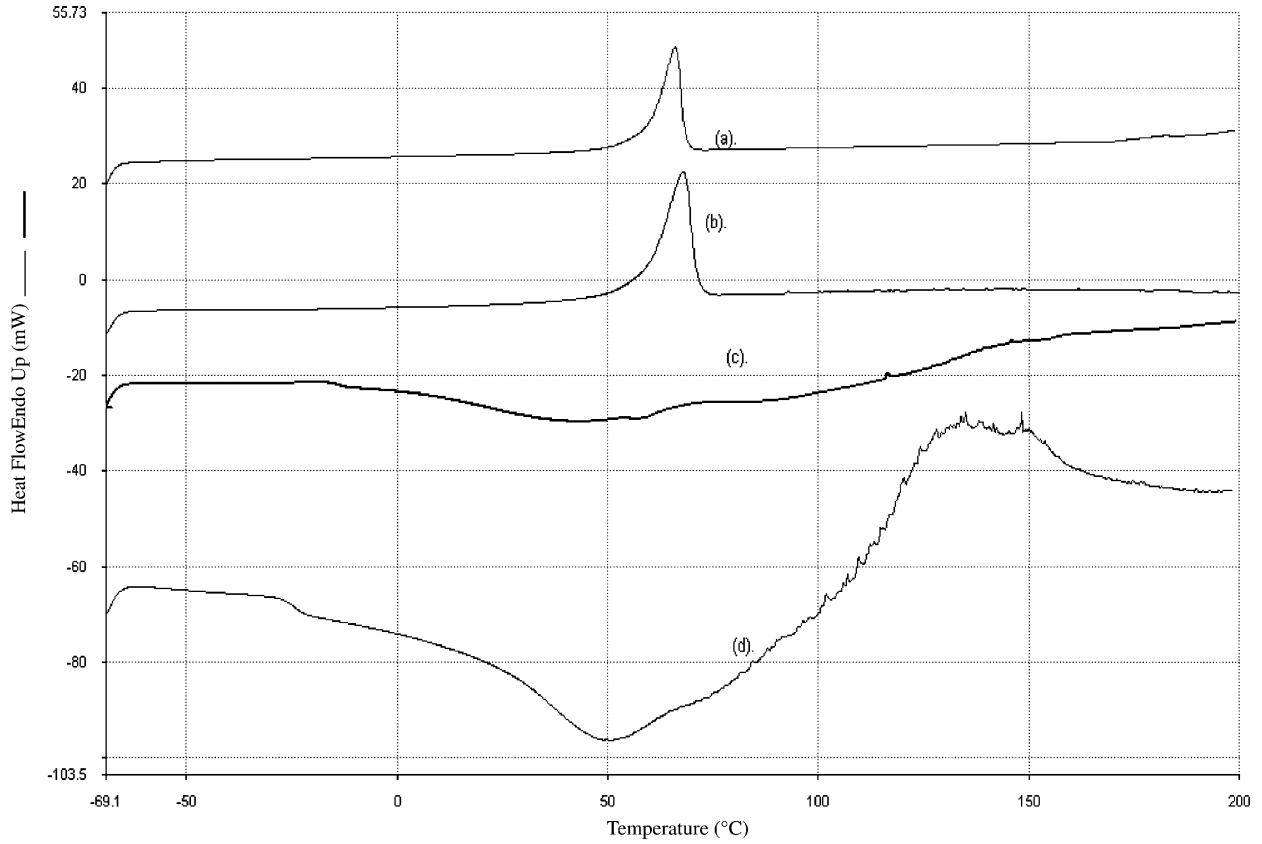


Fig. 1. DSC thermograph for PEO-PVA-KOH electrolyte at various compositions of PEO:PVA—(a) PEO:PVA = 10:0; (b) PEO:PVA = 8:2; (c) PEO:PVA = 5:5; (d) PEO:PVA = 2:8.

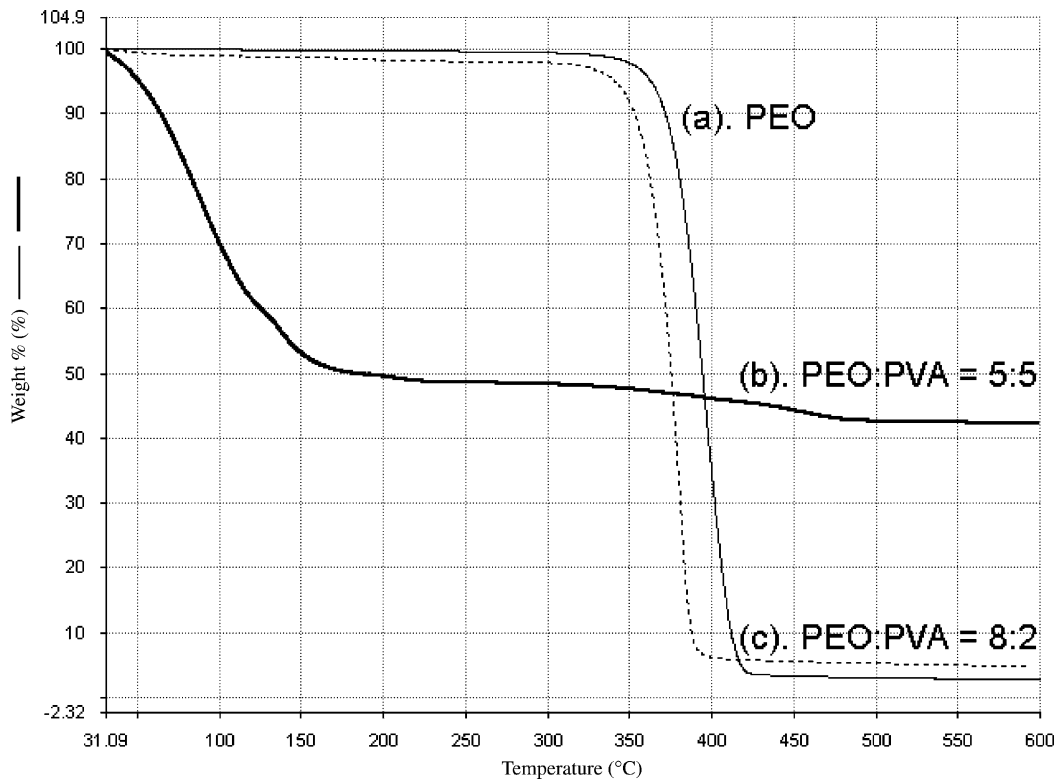


Fig. 2. TGA thermograph for PEO-PVA-KOH electrolyte film at various of ratios PEO:PVA—(a) PEO; (b) PEO:PVA = 5:5; (c) PEO:PVA = 2:8.

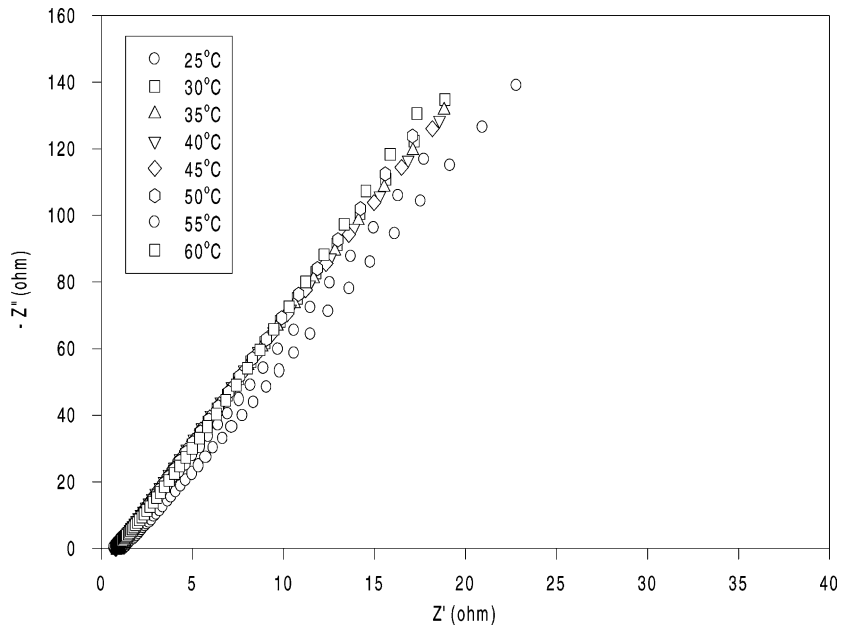


Fig. 3. The ac impedance spectra for PEO–PVA–KOH polymer electrolyte at different temperatures (PEO:PVA = 5:5).

in a single step. In contrast, the PEO–PVA–KOH polymer electrolyte with a high percentage of PVA blending (i.e. PEO:PVA = 5:5) shows a multiple-step degradation. This begins in the region between 60 and 130 °C with a weight loss of 40.4%, and then 9.7% loss when the temperature is above 133 °C. Finally, there is a total weight loss of 57% when the temperature reaches 600 °C.

The ac impedance spectra for the alkaline polymer electrolyte films of PEO–PVA–KOH–H₂O are shown in Fig. 3.

The spectra are for a SS316 | SPE polymer electrolyte | SS 316 cell. Analysis of the spectra yields information about the properties of the electrolyte such as the bulk resistance, R_b (Ω), and the impedance components i.e. double-layer capacitance, C_{dl} , charge-transfer resistance, R_{ct} and Warburg impedance, Z_w (due to the diffusional polarization). Taking into account the thickness of the electrolyte films, the R_b value was converted into the electrolyte conductance, σ ($S\text{ cm}^{-1}$) according to the formula: $\sigma = l/R_b A$. Typically,

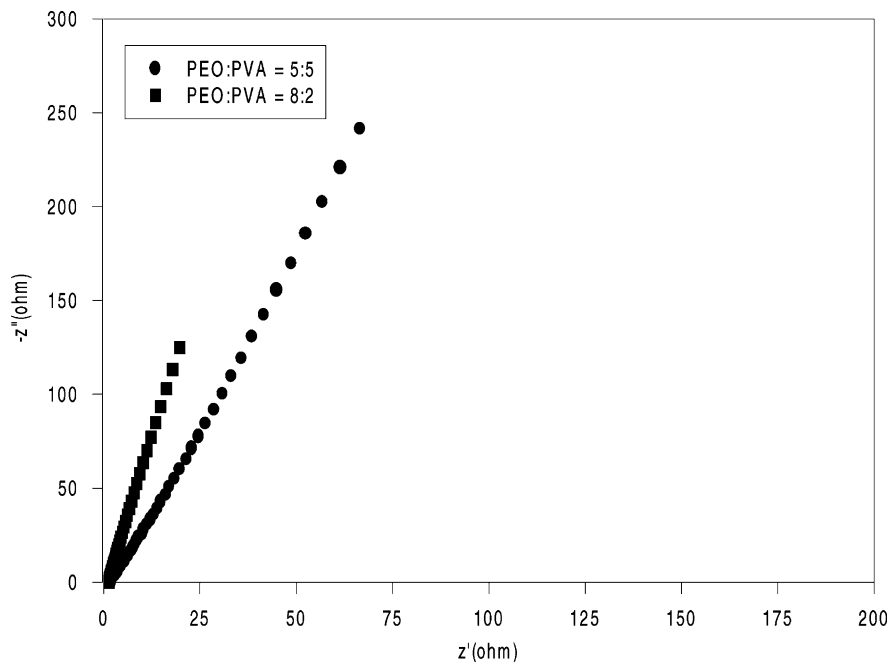


Fig. 4. The ac impedance spectra for PEO–PVA–KOH polymer electrolyte at different ratios of PEO:PVA at room temperature: (a) PEO:PVA:KOH:H₂O = 19.5:19.5:38:23 in wt.% (PEO:PVA = 5:5); (b) PEO:PVA:KOH:H₂O = 30:8:40:22 in wt.% (PEO:PVA = 8:2).

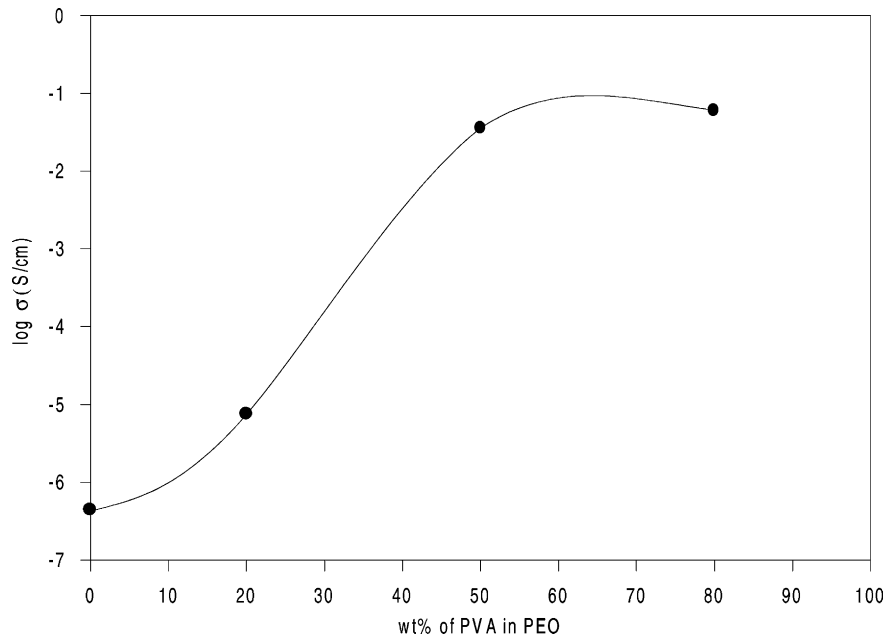


Fig. 5. Ionic conductivity of PEO-PVA-KOH polymer electrolyte with different wt.% of PVA in PEO matrix.

the R_b values for the PEO-PVA-KOH film are of the order of 1–10 Ω and are independent of the KOH content in the films. The corresponding conductivities are between 10^{-1} and 10^{-2} $S\ cm^{-1}$. The ac impedance spectra for PEO-PVA-KOH electrolyte films containing two different amounts of PVA were obtained at room temperature; the results are presented in Fig. 4.

The variation in the conductivity of the polymer electrolyte as a function of the wt.% of PVA in PEO is given in Fig. 5

and Table 2. The data reveal that the conductivity of the PEO-KOH polymer electrolyte is about 10^{-7} $S\ cm^{-1}$ at room temperature and its value increases sharply to 10^{-2} $S\ cm^{-1}$ (i.e. a four-orders of magnitude increase) when the amount of PVA in the PEO matrix is more than 50 wt.%. It is found that there is a rapid rise in conductivity with increasing PVA content.

Several impedance spectra taken over a period of time (8 days) for a SS | SPE polymer electrolyte | SS cell at 25

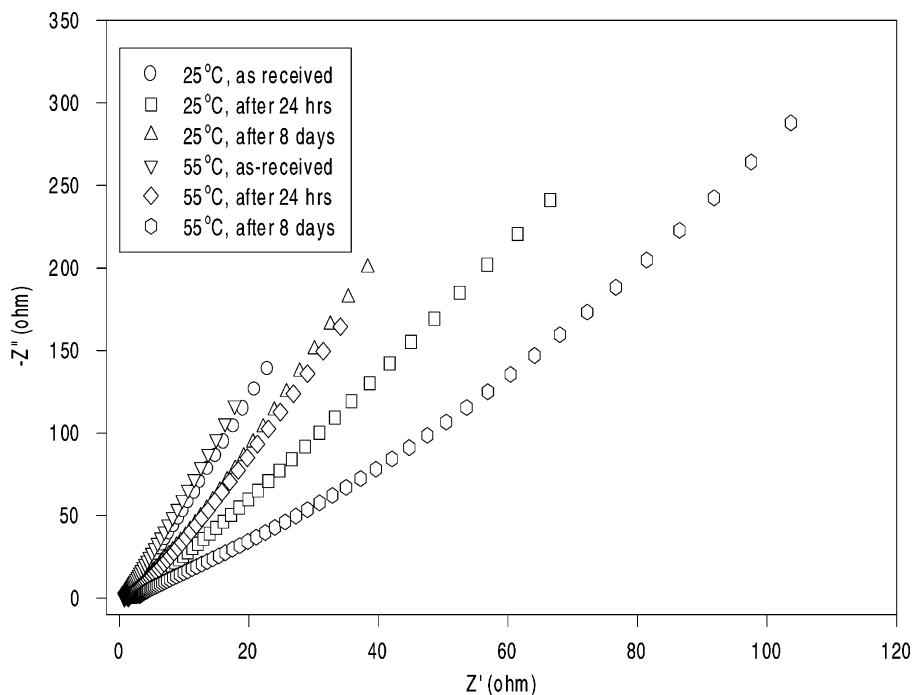


Fig. 6. The ac impedance spectra for PEO-PVA-KOH polymer electrolyte (PEO:PVA:KOH:H₂O = 19.5:19.5:38:23 in wt.%).

Table 2
Conductivity of PEO–PVA–KOH polymer electrolyte for various ratios of PEO:PVA

Temperature (°C)	PEO:PVA (10:0)	PEO:PVA (8:2)	PEO:PVA (5:5)	PEO:PVA (2:8)
25	4.28×10^{-7}	7.43×10^{-6}	0.0577	0.0608
30	4.61×10^{-7}	1.33×10^{-6}	0.0753	0.0704
35	5.23×10^{-7}	6.95×10^{-7}	0.0838	0.0716
40	5.73×10^{-7}	8.16×10^{-7}	0.0910	0.0728
45	5.91×10^{-7}	8.03×10^{-7}	0.0957	0.0734
50	7.31×10^{-7}	8.11×10^{-7}	0.0972	0.0747
55	8.98×10^{-7}	1.06×10^{-6}	0.0993	0.0780
60	9.68×10^{-7}	1.56×10^{-6}	0.1001	0.0860

Table 3
Ionic conductivity (σ) values of PEO–PVA–KOH polymer film after different periods of storage at 25 °C (PEO:PVA:KOH:H₂O = 19.5:19.5:38:23 in wt.%)

Temperature (°C)	σ (S cm ⁻¹)		
	1 h	24 h	8 days
25	0.0577	0.03579	0.03815
30	0.0753	0.05011	0.04159
35	0.0838	0.05684	0.04383
40	0.0910	0.05986	0.04573
45	0.0957	0.06263	0.04631
50	0.0972	0.06442	0.03574
55	0.0993	0.06202	0.02727
60	0.1001	0.07035	0.02300

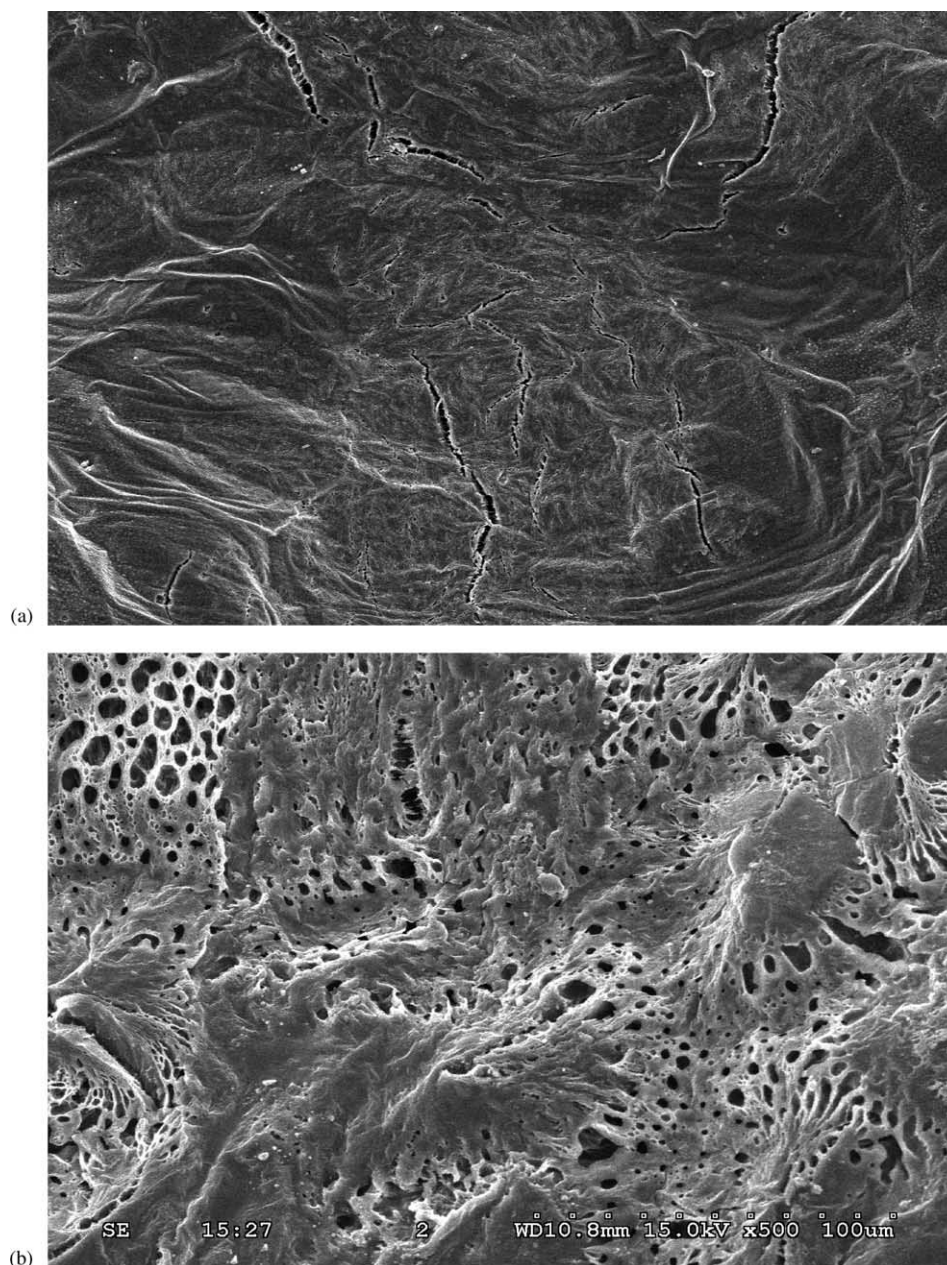


Fig. 7. Electron micrographs of alkaline PEO based polymer electrolyte (PEO:PVA = 5:5; PEO:PVA:KOH:H₂O = 19.5:19.5:38:23 in wt.%): (a) $\times 100$; (b) $\times 500$.

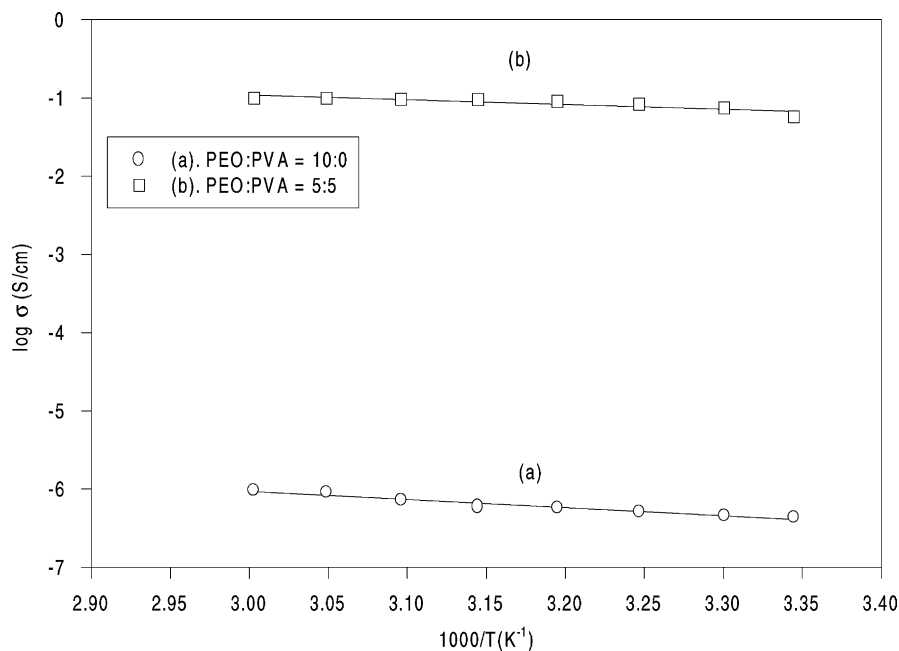


Fig. 8. Arrhenius plot for PEO–PVA–KOH polymer electrolyte at different ratios of PEO:PVA; data from ac impedance analysis.

and 55 °C, are presented in Fig. 6. The ionic conductivity of polymer electrolyte does not change significantly over the entire period of time at the two temperatures, as reported in Table 3. This indicates the absence of any reaction that will lead to a rapid change in ionic conductivity. Thus, it appears that the polymer electrolyte is very stable with on time.

Scanning electron micrographs of the PEO–PVA–KOH polymer film are shown in Fig. 7. The surface of the film contains many small pores of different size. The polymer forms a three-dimension network structure, which allows more KOH electrolyte to be retained. In the absence of pores for the PEO–KOH polymer film, it was observed the surface of the polymer electrolyte is much smooth and less porous.

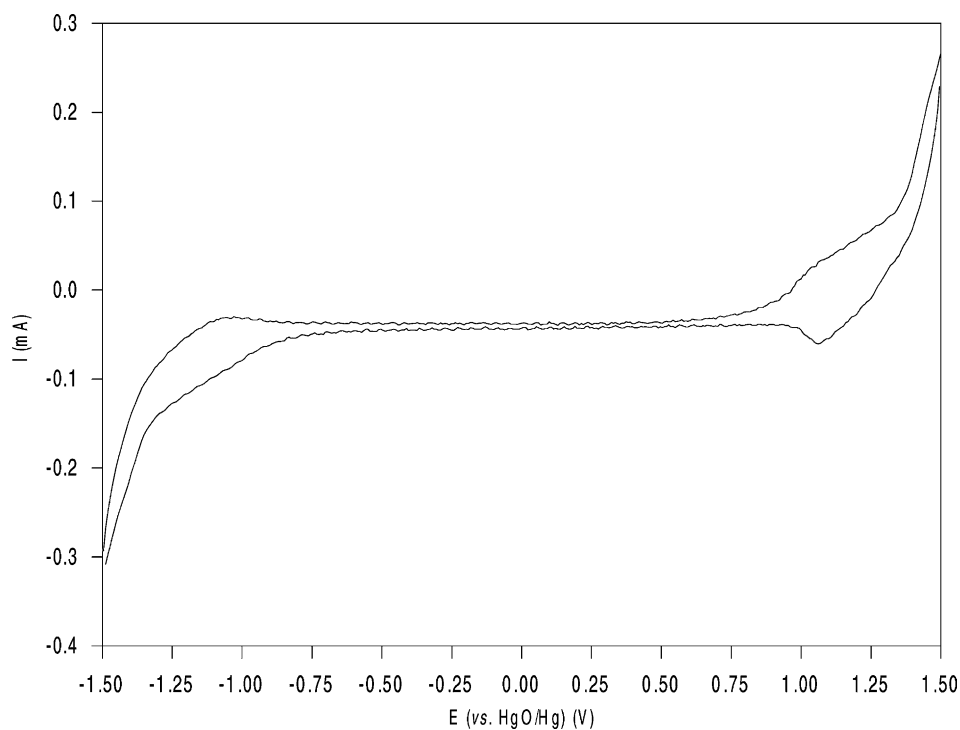


Fig. 9. Cyclic voltammogram of PEO–PVA–KOH polymer electrolyte (PEO:PVA:KOH:H₂O = 19.5:19.5:38:23 in wt.%); scan rate 0.1 mV S⁻¹ at room temperature.

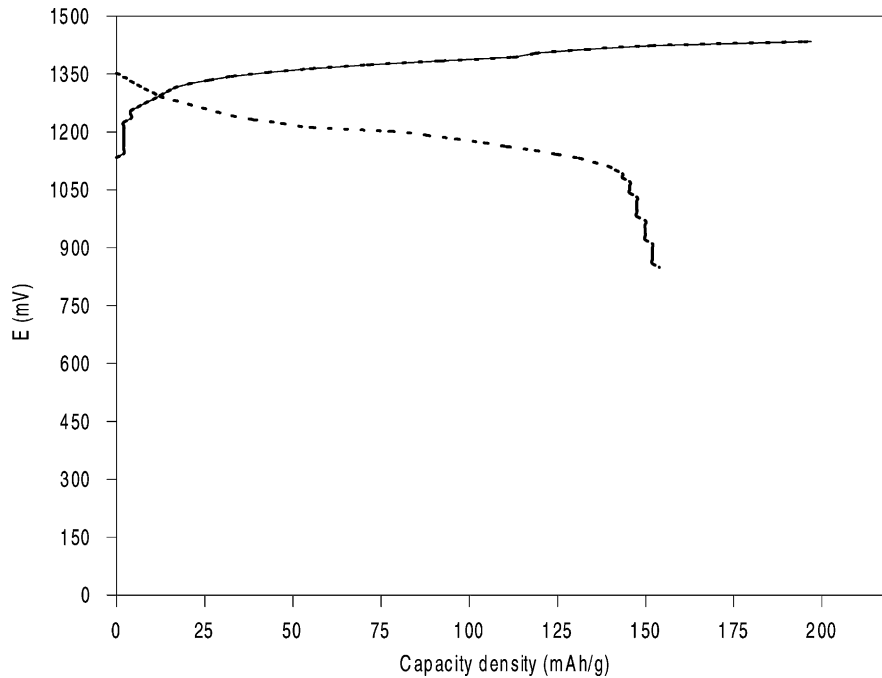


Fig. 10. Charge-discharge curve for a polymer Ni-MH battery containing PEO-PVA-KOH polymer electrolyte, at C/5 rate (PEO:PVA:KOH:H₂O = 19.5:19.5:38:23 in wt.%): capacity, 86 mAh; electrode area, 6 cm²; electrolyte thickness, 0.32 mm.

The temperature dependence of the conductivity is of the Arrhenius type, namely: $\sigma = \sigma_0 \exp(-E_a/RT)$. Linear plots of $\log_{10}(\sigma)$ versus $1/T$, as shown in Fig. 8, gives the activation energy (E_a), which is dependent on the PVA content in the electrolyte film. The E_a for the PEO-KOH-H₂O system is of the order of 20 kJ mol⁻¹. The maximum conductivity (~ 0.10 S cm⁻¹ at 60 °C) is shown by a SPE film with the

composition (wt.%): PEO (19.5):PVA (19.5):KOH (38):H₂O (23), as listed in Table 2.

High conductivity is not sufficient to make the polymer electrolyte suitable for practical battery applications. A broad electrochemical stability window is also important for the practical use of these films. A cyclic voltammogram for the SS | SPE polymer electrolyte | SS cell over the range

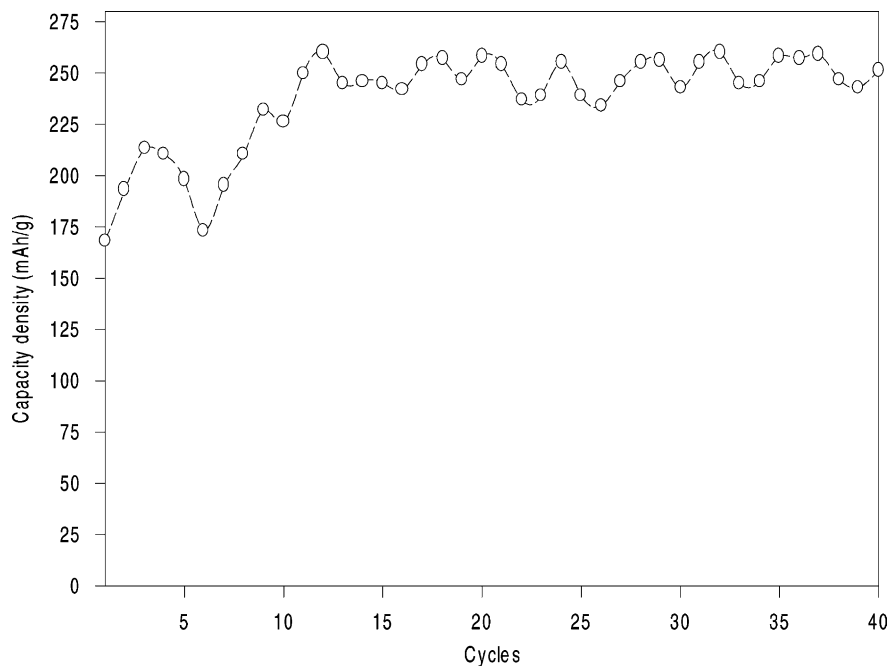


Fig. 11. Cycle life of polymer Ni-MH battery containing PEO-PVA-KOH polymer electrolyte, at C/5 rate (PEO:PVA:KOH:H₂O = 19.5:19.5:38:23 in wt.%): capacity 86 mAh; electrode area, 6 cm²; electrolyte thickness, 0.32 mm.

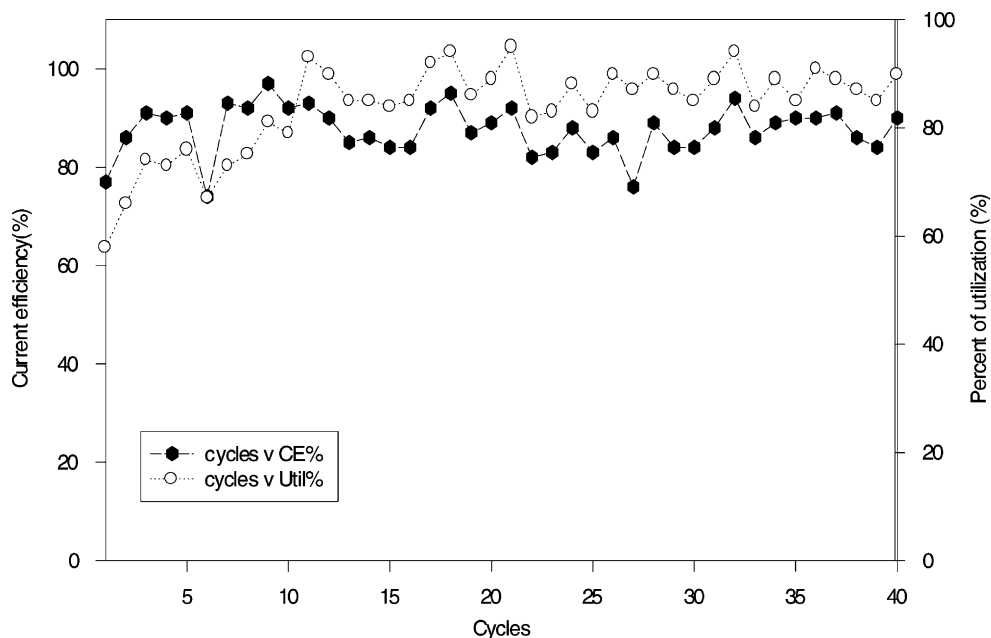


Fig. 12. Current efficiency and percent utilization of polymer Ni–MH battery) containing PEO–PVA–KOH polymer electrolyte at C/5 rate: (PEO:PVA:KOH:H₂O = 19.5:19.5:38:23 in wt.%); capacity, 86 mAh; electrode area, 6 cm²; electrolyte thickness, 0.32 mm.

–1.5 to +1.5 V is shown in Fig. 9. The potential was first scanned in the cathodic direction and then reversed. The electrochemical stability window, defined as a potential region where no appreciable faradic current flows, is limited in its cathodic and anodic parts, where the reduction and oxidation of the polymer electrolyte and OH[–] ions can take place. The stability of the electrolyte at the interface with stainless steel is limited by a potential of about +1.0 V at the anodic side and –1.0 V at the cathodic side. This gives a stability window of about 2.0 V.

A typical charge–discharge curve is presented in Fig. 10. The alkaline polymer Ni–MH cell shows a charge voltage plateau value of 1.35 V and a discharge voltage plateau of 1.20 V. The cycle-life of the cell is shown in Fig. 11. It is observed that the Ni(OH)₂ active material has an average capacity densities of 250 mAh g^{–1} after 15 cycles. The cell capacity is limited by the nickel electrode. The current efficiency of the cell is stable at 80–90% after 10 cycles, as shown in Fig. 12. The average utilization efficiency of the cell is 80%. The theoretical capacity density of Ni(OH)₂ is 289 mAh g^{–1} which is based on the one-electron transfer reaction of Ni(OH)₂ + OH[–] → NiOOH + H₂O + e[–]. The highest capacity density of the cell is about 260 mAh g^{–1} at the C/5 rate.

4. Conclusion

An alkaline PEO–PVA–KOH polymer electrolyte with an ionic conductivity of 10^{–2} S cm^{–1} at room temperature has been fabricated. The polymer electrolyte films have very good mechanical strength and electrochemical stability.

Polymer Ni–MH batteries have been assembled and tested. The cells show good charge and discharge characteristics. It is considered that the PEO–PVA–KOH polymer electrolyte film is a promising candidate for application in all alkaline battery systems.

Acknowledgements

Financial support from the National Science Council, Taiwan, ROC (Project No. NSC-89-2214-E-131-001) is gratefully acknowledged.

References

- [1] F.M. Gray, Solid Polymer Electrolytes—Fundamental and Technological Application, VCH, New York, 1991.
- [2] D.E. Fenton, J.M. Parker, P.V. Wright, *Polymer* 14 (1973) 589.
- [3] P.V. Wright, *Br. Polym. J.* 7 (1975) 319.
- [4] M.B. Armand, J.M. Chabagno, M.J. Duclot, in: M.J. Duclot, P. Vashishta, J.M. Mundy, G.K. Shenoy (Eds.), *Fast Ion Transport in Solids*, 1979.
- [5] J.F. Fauvarque, S. Gunot, N. Bouzid, E. Salmor, J.F. Penneau, *Electrochim. Acta* 40 (1995) 2449.
- [6] S. Gunot, E. Salmon, J.F. Penneau, F. Fauvarque, *Electrochim. Acta* 43 (1998) 1163.
- [7] N. Vassal, E. Salmon, F. Fauvarque, *Electrochim. Acta* 45 (2000) 1527.
- [8] N. Vassal, E. Salmon, J.F. Fauvarque, *J. Electrochem. Soc.* 146 (1999) 20.
- [9] F. Lichtenberg, K. Kleinsorgen, *J. Power Sources* 62 (1996) 207.
- [10] L. Hui, D. Yunchang, Y. Jiongliang, W. Zeyun, *J. Power Sources* 57 (1995) 137.
- [11] X. Wang, J. Yan, H. Yuan, Z. Zhou, D. Song, Y. Zhang, L. Zhu, *J. Power Sources* 72 (1998) 221.

- [12] C. Shaoan, Y. Anbao, L. Hong, Z. Jianqing, C. Chunan, *J. Power Sources* 76 (1998) 215.
- [13] J. Kuklinski, P.G. Russell, *J. Power Sources* 76 (1998) 11.
- [14] D. Yunchang, Y. Jiongliang, C. Zhaorong, *J. Power Sources* 69 (1997) 47.
- [15] Y. Sasaki, T. Yamashita, *Thin Solid Films* 334 (1998) 117.
- [16] C.Z. Yu, W.H. Lai, G.J. Yan, J.Y. Wu, *J. Alloys Compounds* 293/295 (1999) 784.
- [17] D. Yan, J. Wang, *J. Alloys Compounds* 293/295 (1999) 775.
- [18] Z. Chang, Y. Zhao, Y. Ding, *J. Power Sources* 77 (1999) 69.
- [19] M. Oshitani, M. Watada, K. Shodai, M. Kodama, *J. Electrochem. Soc* 148 (2001) A67–A73.