

# Cationic polysulfonium membrane as separator in zinc–air cell

Eniya Listiani Dewi, Kenichi Oyaizu, Hiroyuki Nishide, Eishun Tsuchida\*

*Polymer Laboratory, Department of Applied Chemistry, Advanced Research Institute for Science & Engineering,  
Waseda University, Tokyo 169-8555, Japan*

Received 7 October 2002; accepted 28 November 2002

## Abstract

A polyelectrolyte containing a sulfonium cation, poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene trifluoromethanesulfonate) (**1**) was tested as a separator in a zinc–air cell. In comparison with the commercially available separators such as polypropylene, polysulfonium **1** was highly effective to prevent cation permeation from the anode to cathode and effectively increased the capacity six-fold greater than that of polypropylene during discharge. This phenomenon was explained by the ion-exchange process of the membrane **1**, which showed an anion-permselectivity toward  $\text{OH}^-$  at low KOH aqueous solution concentrations (<1 M).

© 2003 Elsevier Science B.V. All rights reserved.

*Keywords:* Cationic polyelectrolyte; Polysulfonium; Separator; Anion permselectivity; Zinc–air battery

## 1. Introduction

Significant efforts to develop components for the metal–air battery (overall reaction:  $(4/x)\text{M} + \text{O}_2 + 2\text{H}_2\text{O} = (4/x)\text{M}(\text{OH})_x$ ) have been made by many researcher, such as the rechargeable zinc–air battery [1,2], zinc corrosion [3], gas diffusion electrode and oxygen catalyst [4–6]. In contrast to their work, the material development of the separators has been very limited in metal–air batteries, although more novel electrochemical processes are being developed and require a membrane or separator to play an integral function in the entire process especially in alkaline batteries. The commonly used separators are porous membranes such as polyethylene, polyvinyl alcohol, polyolefin and polypropylene [7–11]. The separator in a zinc–air battery is usually a polypropylene membrane such as Celgard<sup>®</sup> with the porosity of 10–20  $\mu\text{m}$ .

The function of the separator is to prevent cross-mixing of the positive and negative electrolytes but to still allow the transport of ions for completion of the circuit during the passage of current. Due to its porosity, the cationic compound produced in the anode reaction,  $\text{Zn}^{2+}$  ( $\text{Zn} + 2\text{OH}^- = \text{Zn}(\text{OH})_2 + 2\text{e}^-$ ;  $E_0 = -1.25$  V versus SHE) can easily pass through the separator to cathode that leads to an increased polarization and decreased capacity and battery life [2,12]. Herein, we focus this study on the prevention of the anion

transfer process in the zinc–air battery cell using a cationic polyelectrolyte membrane in order to provide an increased of capacity and longer discharge performance. The purpose of this study was to improve the understanding of anion exchange by the polysulfonium cation (poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene trifluoromethanesulfonate)) **1** and study the polysulfonium membrane as a new type of separator in a zinc–air battery.

## 2. Experimental

### 2.1. Materials

Polysulfonium **1** ( $M_n = 4.3 \times 10^4$ ,  $M_w = 2.4 \times 10^5$ ) was synthesized according to previous procedures as already described [13,14]. The resulting polysulfonium was soluble in acetonitrile, therefore, this solvent was used to dissolve the polysulfonium **1** in all the experiments of permselectivity measurements.  $\text{K}_4\text{Fe}(\text{CN})_6$  purchased from the Kanto Chem. Co., was purified by crystallization in the usual manner, and the other chemicals for the supporting electrolyte were commercially available reagent grade and were used without purification. A thin film of polysulfonium **1** was prepared by dissolving **1** in acetonitrile and spread on a Teflon plate in order to slowly evaporate in air to make a 30  $\mu\text{m}$  thick transparent membrane. The polypropylene type separator Celgard<sup>®</sup> 5550 with a thickness of 114  $\mu\text{m}$  was a gift from Celgard<sup>®</sup> Inc. Zinc powder (99.9% grade) was purchased

\* Corresponding author. Tel.: +813-5286-3120; fax: +813-3205-4740.  
E-mail address: [eishun@mn.waseda.ac.jp](mailto:eishun@mn.waseda.ac.jp) (E. Tsuchida).

from Kanto Chem. The carbon paste electrode ( $\varnothing$  2 cm, 1.5 g) with a treated  $\text{MnO}_2$  catalyst was used as the air cathode which was a kind of gift from Matsushita Elec. Co.

## 2.2. Apparatus and procedure

The electrochemical instrumentation for the modified electrode investigations included a Nikko Keisoku DPGS-1 dual potentiogalvanostat, NFG-3 universal programmer and a Graphtec WX2400 X–Y recorder to obtain the voltammogram. The modified electrode and electrolytes were setup in a conventional two-compartment cell in which a glassy carbon disk electrode ( $0.28 \text{ cm}^2$ ) served as the working electrode, the counter electrode was a platinum wire and the reference electrode was a saturated calomel electrode (SCE).

The modified electrode was mounted as previously described with the following slightly modification [15]. The polysulfonium coatings employed in the electrochemical experiments were prepared using  $5 \mu\text{l}$  of a 1 mM solution of the polysulfonium in acetonitrile placed on a glassy carbon disk and the solvent then allowed to slowly evaporate in air. The triflate counterions initially present in the coatings were removed by transferring the electrode to a 1 mM solution of  $\text{K}_4\text{Fe}(\text{CN})_6$  with 0.1 M  $\text{CH}_3\text{SO}_3\text{Na}$  which is the most suitable supporting electrolyte to make an ionic-exchange reaction [15]. The electrode potential was cycled over the oxidation and reduction waves of anion ( $-0.4$ – $0.6 \text{ V}$  versus SCE) for 10 min at the rate  $25 \text{ mV}$  until the desired amount was incorporated into the coating by ion exchange. The electrode was then removed and transferred to a pure supporting electrolyte solution (KOH) for the permselectivity measurements. Experiments were conducted under air at  $25 \text{ }^\circ\text{C}$ . The potentials were measured and are reported with respect to a SCE.

For the zinc–air cell discharge test, the electrolyte was 2 ml of 1 M KOH. The separators were polysulfonium **1** and Celgard<sup>®</sup> 5550 ( $\varnothing$  2.6 cm). The separators were sandwiched between the Zn anode and air cathode electrode. A Hokuto Denko Discharge analytical instrument was used to measure the electrical discharge characteristics of the test cells at a 1 mA discharge current under ambient conditions. The compartment cell ( $\varnothing$  2.6 cm inner size and  $\varnothing$  3.6 cm outer size) was manually constructed with oxygen flowing on the oxygen electrode side.

## 3. Results and discussion

### 3.1. Permselectivities of polysulfonium

In previous report, the quantitative analysis of the influence of the supporting electrolyte concentration on the apparent formal potentials of the redox reactants incorporated as probes in the polyelectrolyte coatings was presented for  $\text{CH}_3\text{SO}_3\text{Na}$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaHPO}_4$ ,  $\text{CF}_3\text{SO}_3\text{Na}$ , etc. [15]. A subsequent measurement of the quantity of

$\text{Fe}(\text{CN})_6^{4-}$  remaining in the coating showed that no more than 5% was lost during the slow potential scan by cyclic voltammetry. It has a stable and reversible response that was obtained in the  $\text{CH}_3\text{SO}_3\text{Na}$  supporting electrolyte, which was employed for most of the measurements to incorporate the ferricyanide. The cationic polyelectrolyte **1** has been employed to confine the ferricyanide ion to the electrolyte surface from the electrolyte solutions, which resulted in an increase in the apparent current due to the binding of  $\text{Fe}(\text{CN})_6^{3-}$  and the methylsulfonio moieties in **1**. The permselectivities of coating membrane with the incorporated ferricyanide was prepared in the usual manner as previously described [15,16]. The electroactive couples of  $\text{Fe}(\text{CN})_6^{3-/4-}$  incorporated in the modified electrode surface served as redox probes whose apparent formal potentials ( $E_{\text{app}}$ ) changed as the concentration of the supporting electrolyte of KOH varied as shown in Fig. 1 (top).

The magnitude of these changes is summarized in Fig. 1 (bottom). The  $E_{\text{app}}$  of the  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox couple decreased as the concentration of  $\text{OH}^-$  increased between 0.05 mM and 1 M. For an ideal anion-permselective coating,  $E_{\text{app}}$  is changed by  $-59 \text{ mV}$  at  $25 \text{ }^\circ\text{C}$  for every decade change in the concentration of the electrolyte consisting of the monoanion  $\text{OH}^-$  [17]. The redox potential obeys the

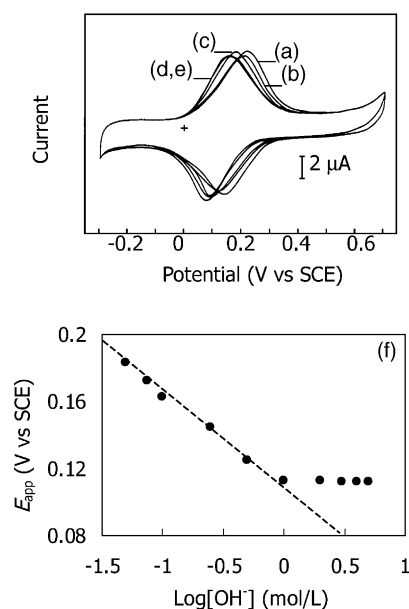


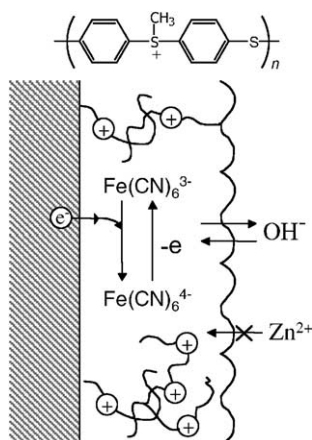
Fig. 1. Cyclic voltammogram of glassy carbon electrode coated with **1** containing  $\text{Fe}(\text{CN})_6^{3-/4-}$  and recorded in various concentrations of pure KOH electrolyte: (a) 0.05 mol/l, (b) 0.075 mol/l, (c) 0.25 mol/l, (d) 1 mol/l, (e) 3 mol/l. The oxidation and reduction of the  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Fe}(\text{CN})_6^{3-}$  incorporated in a coated polymer **1** when the electrode potential was stepped from  $-0.1$  to  $+0.3 \text{ V}$  and then back to  $-0.1 \text{ V}$ . (f) Apparent formal potentials of the  $\text{Fe}(\text{CN})_6^{3-/4-}$  couple incorporated in **1** as a function of the concentration of  $\text{OH}^-$ .  $E_{\text{app}}$  are the averages of the anodic and cathodic peak potentials in the cyclic voltammograms of the above experiments. The slope of the best-fit line (in mV per decade) is  $-56$ . The incorporated ferricyanide on the coated electrode was  $4.3 \times 10^{-4} \text{ mol/cm}^2$ . Glassy carbon electrode area:  $0.28 \text{ cm}^2$ . Electrolyte:  $\text{H}_2\text{O}$  containing KOH as supporting electrolyte. Scan rate:  $25 \text{ mV/s}$ .

Nernst equation calculated from Fig. 1,  $E_{app}$  (V) = 0.11 – 0.056 log[OH<sup>-</sup>], 0.05 < [OH<sup>-</sup>] < 1 (M). For a high concentration over 1 M KOH, the apparent potential did not slightly decreased due to the shielding of the sulfonium cation. The deviated slopes obtained using the OH<sup>-</sup> indicated that the polysulfonium **1** has an ideal permselectivity and suggest that the ionic-exchange only takes place at concentration not more than 1 M KOH.

### 3.2. Discharge performance

As a new application of this polycation membrane, we try to use the anion-exchange membrane **1** in metal–air batteries as a separator in order to stop the cationic compound as a side product on the anode side of battery. The fact that a metal cation from the anode reaction (Zn<sup>2+</sup>) would not crossover, the cationic membrane, was determined using the modified glassy carbon electrode of **1** without any incorporation of ion. In the electrolyte containing 1 M KOH and 1 mM Zn(OH)<sub>2</sub>, the modified electrode **1** has no peak observed in the cyclic voltammogram, as illustrated in Scheme 1.

For application in batteries, polysulfonium **1** (30 μm) was combined with zinc and an air electrode, which was treated with an MnO<sub>2</sub> catalyst, and discharged at different electrolyte concentrations. As shown in Fig. 2, a current increase of approximately six-fold for the polysulfonium separator (0.6 V, 124.8 h, 86.4 mAh/g) versus the polypropylene separator (1.32 V, 70.5 h, 14.5 mAh/g) was determined by the discharge analysis in an electrolyte of 1 M KOH. The current capacities of the discharged cells with various concentrated electrolytes were plotted as shown in Fig. 3. The increasing capacity versus the electrolyte was only observed at concentrations not higher than 1 M of KOH where in the concentration on 5, 8 and 10 M of KOH, the current capacities of the cell have the same value as the other cells with Celgard<sup>®</sup> as the separator. The polysulfonium membrane **1** showed a high ionic selectivity and prevented cation permeation to the cathode electrode that increased the overall capacity of the zinc–air cells. Although the average voltage



Scheme 1. Scheme of modified electrode using polysulfonium **1**.

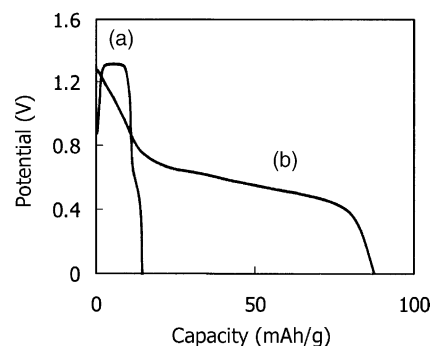


Fig. 2. Discharge capacity for zinc–air battery with (a) Celgard<sup>®</sup> 5550, (b) polysulfonium **1** membrane as separator. Carbon paste that contained MnO<sub>2</sub> catalyst was used in cathode electrode and combined with 2 ml of 1 M KOH and 1 g of zinc anode. The cells were discharged at 1 mA at room temperature.

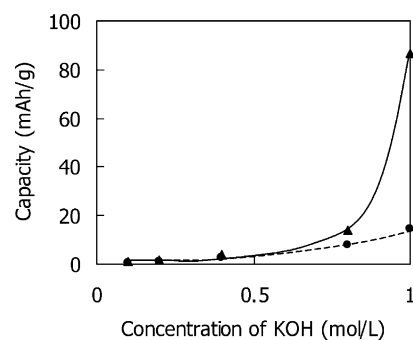


Fig. 3. Capacities of discharge cell depend on the concentration of the KOH electrolyte. The cell conditions are described in Fig. 2. The solid line is the discharge capacity with polysulfonium **1**, and the dash line is for Celgard<sup>®</sup> 5550.

of the zinc–air cell was low due to the high resistance of the polysulfonium **1** (203 Ω),<sup>1</sup> the discharge time was very high compared to the Celgard<sup>®</sup> ones with a low concentration of electrolyte.

## 4. Conclusions

Metal–air batteries have a high theoretical energy density of 1085 Wh/kg based on the molecular weight of ZnO (658 Wh/kg) and the theoretical cell voltage of 1.65 V, but the output power density is very low (<50%) and the lifetime is short due to the activity of the oxygen catalyst and the crossover of the anion to the other electrode [2,12]. Hence, it appears that an ion selective polysulfonium **1**, poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate) membrane, has acceptable separator properties and performs with high anion selectivity due to high diffusion coefficient of the anion than that of the commercially separators to which it

<sup>1</sup> The resistance measurements were done using a K-705RS Kyowariken resistance instruments, with 1 M KOH immersed and dried before the analysis.

was compared. Polysulfonium can be a good material as the separator of a zinc–air battery, which is placed between the cathode and zinc anode, because the self-discharging process through the permeation of the zinc cation is completely prevented by the anion permselective material under basic conditions. When designing zinc–air cell, with a thickness of almost 75% less compared to commercially available ones, it is possible to reduce the cell thickness. This behavior was interpreted as a good characteristic of the polysulfonium **1**, and can successfully increase the discharge current of the batteries by almost six times.

### Acknowledgements

E.L. Dewi acknowledges Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists (DC1-2000, no. 05709).

### References

- [1] J. Goldstein, I. Brown, B. Koretz, *J. Power Sources* 80 (1999) 171.
- [2] F. Beck, P. Ruetschi, *Electrochim. Acta* 45 (2000) 2467.
- [3] A.R.S. Kannan, S. Muralidhran, K.B. Sarangpani, V. Balaramachandran, V. Kapali, *J. Power Sources* 57 (1995) 93.
- [4] M. Maja, C. Orecchia, M. Strano, P. Tosco, M. Vanni, *Electrochim. Acta* 46 (2000) 423.
- [5] Z. Wei, W. Huang, S. Zhang, J. Tan, *J. Power Sources* 91 (2000) 83.
- [6] N. Li, X. Yan, W. Zhang, B. Lin, *J. Power Sources* 74 (1998) 255.
- [7] T. Wada, T. Hirashima, *J. Power Sources* 107 (2002) 201.
- [8] S.H. Choi, H.J. Kang, E.N. Ryu, K.P. Lee, *Rad. Phys. Chem.* 60 (2001) 495.
- [9] L.C. Hsu, W. Sheibley, *J. Electrochem. Soc.* 129 (1982) 251.
- [10] D.W. Sheibley, M.A. Manzo, O.D. Sanabria, *J. Electrochem. Soc.* 130 (1983) 255.
- [11] I. Kaur, B.N. Misra, S. Kumar, *J. Appl. Polym. Sci.* 69 (1998) 143.
- [12] K. Kinoshita, *Electrochemical Oxygen Technology*, Wiley, New York, 1992.
- [13] E. Tsuchida, E. Shouji, K. Yamamoto, *Macromolecules* 26 (1993) 7144.
- [14] E. Tsuchida, K. Yamamoto, K. Miyatake, Y. Nishimura, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 23.
- [15] K. Oyaizu, H. Nakano, J. Natori, E. Tsuchida, *J. Electroanal. Chem.* 498 (2001) 232.
- [16] E.L. Dewi, H. Nakano, K. Oyaizu, H. Nishide, E. Tsuchida, *J. Macromol. Sci., Pure Appl. Chem.* A40 (2003) 37–47.
- [17] A.J. Bard, L.R. Faulker, *Electrochemical Method Fundamentals and Applications*, 2nd ed., Wiley, New York, 2000, p. 580.