



## Short communication

## Effects of ionomer films on secondary alkaline zinc electrodes

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**Abstract**

Three low cost zinc-ionomers that are directly in contact with zinc electrodes are found to greatly impede the dissolution of zinc discharge products into electrolyte. This reduces the dendritic growth and shape change of the zinc electrodes. Discharge experiments with constant current, anodic polarization experiments and charge–discharge studies are carried out to assess the performance of these ionomers. Scanning electron microscopy is also applied to examine the morphology of the surface of the zinc electrodes before and after 50 charge–discharge cycles. © 1998 Elsevier Science S.A. All rights reserved.

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**1. Introduction**

Widespread commercialization of zinc-anode batteries has been prevented by the short cycle life of the zinc electrode. In general, the shape change of zinc electrode and dendritic growth, which both result from the high solubility of zinc discharge products in the electrolyte, are the main problems. The deposition of zinc active material during charging is non-uniform, and thus electrode shape change occurs and dendritic deposits are formed due to the high local current density. Attempts to reduce the solubility of zinc discharge products during discharging and to obtain a uniform zinc deposit during charging have included the use of additives in either the electrode [1–8] or the electrolyte [9–14]. The use of such additives may, however, bring about some disadvantages. For example, the use of electrode additives, such as  $\text{Ca}(\text{OH})_2$  [1,15–17], will reduce the initial content of zinc active species in the zinc electrode and thus will lower the specific energy. Some electrolyte additives may lower the specific power of the zinc electrode or affect the performance of the positive electrode in zinc batteries. It is therefore necessary to find a better solution to limiting the amount of the discharge products that pass into the alkaline electrolyte. In this respect, lanthanum and neodymium hydroxides, which are coated on the zinc electrode, are found to be effective

[18]. In the present work, an ionomer film which is substantially in direct contact with the zinc electrode is studied.

Ionomers are ion-containing polymers, typically with hydrocarbon backbones, that contain a relatively small number of acid groups. These acid groups are incorporated into the main chain or are present as pendant groups. Although ionomers contain only 15 mol% or less of ionic comonomer, the ionic groups have a major effect on material properties [19]. It has been proposed [20], and by now generally accepted, that these effects result from aggregation of the ions into microdomains, which act as physical crosslinks in the material.

In this paper, a low cost zinc-ionomer derived from styrot-acrylic acid copolymer which is synthesized in laboratory has been used in zinc electrodes. These zinc-ionomers display excellent film formation and excellent stability in alkaline solution. The following zinc-ionomers are used in this work: (A) P(St-coAA-4.83)-Zn-100; (B) P(St-co-AA-8.55)-Zn-100; (C) P(St-co-BA-co-AA-4.83)-Zn-100; where: P = Poly; St = styrot; AA = acrylic acid; BA = butyl acrylate; 4.83 and 8.55 = the molar content of acrylic acid in copolymer; 100 = the degree of neutralization. The purpose of the introduction of BA into the material is to enhance further the adhesive force between the ionomer layer and zinc electrode. With all ionomers,  $\text{Zn}(\text{OAc})_2$  was used as the source of  $\text{Zn}^{2+}$  cations when the copolymers were neutralized.

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The aim of this study is to examine the effects of a given zinc-ionomer film which is in direct contact with the zinc electrode, on the polarization performance, dendritic growth and shape change of zinc electrodes.

## 2. Experimental

### 2.1. Preparation of zinc electrodes

Teflon-bonded porous zinc electrodes containing 85 wt.% Zn, 10 wt.% ZnO and 5 wt.% PTFE, were fabricated. A silver-plated copper mesh was used as the current-collector in these electrodes. The electrodes had an apparent area of 1 cm<sup>2</sup>.

Planar zinc electrodes (99.999% Pure; area: 1 × 1 cm; Johnson Matthey Chemicals, Royston, UK) were pre-treated in acetone (degreasing) followed by a short immersion in 50% HCl (v/v, sp. gr. 1.18) until a light, matt, clean surface was obtained.

### 2.2. Preparation of ionomer films

Solutions of ionomers (2 wt.%, fully dried) were prepared by dissolving ionomers into tetrahydrofuran (THF) solvent (AR,  $d = 0.888$ , Yixin Chemical Reagent Factory, Jiangsu Province, China). The solutions were colourless and transparent.

The ionomer films coated on zinc electrodes were prepared by dipping zinc electrodes (porous or planar) in the abovementioned solution of ionomer, and then removing the electrodes and drying them in air. The ionomer films were formed on the electrodes through the removal of THF.

### 2.3. Discharge experiments

Discharge experiments (constant current) were performed in a cell with a porous zinc anode ('blank' or coated with ionomer film) and an NiOOH cathode. The electrolyte was a 30% KOH solution. The concentrations of zincate in the electrolyte were determined in situ by an electrochemical method after the zinc electrodes were discharged.

### 2.4. Anodic polarization experiments

Anodic polarization curves were measured from the rest potential of the zinc electrode to  $-1.14$  V at the scanning rate of  $1 \text{ mV s}^{-1}$  with a RDE4 bipotentiostat (Pine Instruments, USA) connected to a Type 3086  $x$ - $y$  recorder (Yokogama Hokushin Electric, Tokyo, Japan) in a cell which comprised a porous zinc electrode ('blank' or coated with ionomer film), a platinum sheet counter electrode, and a Hg/HgO reference electrode. Before the polariza-

tion experiments, the ZnO in electrodes were reduced to zinc by charging with constant current.

### 2.5. Charge-discharge experiments

An analog cell (flooded electrolyte) with a zinc anode ('blank' or coated with ionomer film) and an NiOOH cathode was used. The electrolyte was 30% KOH saturated with zincate. This was prepared by dissolving ZnO powder (AR, Chengdu Chemical Reagent Factory, Chengdu, China) in 30% KOH; the amount of ZnO was sufficient to saturate the solution with zincate. The cells were discharged at  $40 \text{ mA cm}^{-2}$  for 6 min, followed by charging at  $20 \text{ mA cm}^{-2}$  for 12 min, and were reversed automatically when the time set for discharge (or charge) was completed.

### 2.6. Scanning electron microscopy

The preparation of samples for study by scanning electron microscopy (SEM) was as follows. The zinc electrode (50th cycle, charged state) was removed immediately from the electrolyte, washed repeatedly with double-distilled water, rinsed in acetone, and dried in air.

## 3. Results and discussion

### 3.1. Discharge experiments

The concentration of zincate in the electrolyte after each porous zinc electrode ('blank' or coated with ionomer film) was discharged with constant current are illustrated in Table 1. It can be seen that the zincate concentrations after discharge of zinc electrodes coated with ionomer films are much lower than that for a 'blank' electrode. Apparently, the appearance of zincate in the electrolyte results from the dissolution of zinc discharge products. In essence, the lower the concentration of zincate in the electrolyte, the less the dissolution and migration of the zinc discharge product into the electrolyte. Thus, the amount of soluble zinc discharge product can be reduced when zinc-ionomer layers are coated on zinc electrodes. It was proposed and widely accepted [3] that if the amount of zinc dissolved in the electrolyte is decreased, the rate of zinc redistribution (shape change) will be decreased. For the above reasons, it can be concluded that the ionomer film coated on zinc electrode can reduce zinc dendritic growth and zinc electrode shape change.

The behaviour of ionomer films on zinc electrodes may be attributed to the existence of microdomains formed by the aggregation of the ions in ionomers. Therefore, when the ionomer films are substantially in direct contact with zinc electrodes, the migration of  $\text{Zn}(\text{OH})_4^{2-}$  anions (which have a relatively larger ionic radius) toward the electrolyte can be mechanically impeded. Moreover, because the ionic groups in the ionomers are anions ( $-\text{COO}^-$ ) and, there-

Table 1  
Concentration of zincate in electrolyte after discharge of zinc electrodes

Electrode	'Blank'	Coated with A ionomer film	Coated with B ionomer film	Coated with C ionomer film
Concentration of zincate ( $\text{mol l}^{-1}$ )	0.20	0.09	0.05	0.07

fore, repel the negative charge-loaded  $\text{Zn}(\text{OH})_4^{2-}$  anions, it is difficult for  $\text{Zn}(\text{OH})_4^{2-}$  anions to migrate from the zinc electrode to electrolyte.

The ionomers (A, B and C) used in this work have been described in Section 1. The data in Table 1 also indicate that a coating of B ionomer film is more effective in preventing the elution of  $\text{Zn}(\text{OH})_4^{2-}$  anions into electrolyte than a coating of either A or C ionomer. This phenomenon may result from the higher molar content of carboxylic anion ( $-\text{COO}^-$ ) in the B ionomer, which impedes  $\text{Zn}(\text{OH})_4^{2-}$  anions from migrating toward the electrolyte more than A or C ionomer, and causes the change of coordinate form of  $\text{Zn}^{2+}$  in the ionomer, which also may increase the limitation of the migration of  $\text{Zn}(\text{OH})_4^{2-}$  toward electrolyte.

### 3.2. Anodic polarization experiments

Anodic polarization experiments were performed in order to study the effects of ionomer on the performance of porous zinc electrodes. The resulting curves for porous zinc electrodes ('blank' and coated with A, B or C ionomer) are shown in Fig. 1. The apparent current density for electrodes with A, B or C ionomer films is larger than that for a 'blank' electrode over the whole polarization potential range, i.e., from the rest potential of the electrode to  $-1.14$  V. These differences are more obvious during the

initial stage of polarization and indicate that the performance of porous zinc can be greatly improved by coating with A, B or C ionomer films, especially during the initial stage of polarization.

The use of porous electrodes in batteries is to increase greatly the active specific surface for electrochemical reaction. In a porous electrode, the electrode reaction takes place in a three-dimensional spatial structure. Thus, the polarization varies at different depths remote from the electrode surface. That is to say, the interior surface of the electrode cannot be fully utilized because of the electrolyte concentration and the potential gradients in the inner part of the electrode. This limits the effectiveness of porous electrodes to some degree. With a Teflon-bonded porous zinc electrode, the addition of PTFE may increase the hydrophobicity of the electrode, and this effect may be more pronounced on the inner surface of electrode. Because the zinc electrodes coated with ionomer films are prepared by directly dipping porous electrodes in solutions of the ionomers (see Section 2.2), the films can form not only on the external surface but also on the inner surface of the porous electrode when electrodes are dried in air. It is probable that the ionic group ( $-\text{COO}^-$ ) which is uniformly spread in the ionomer films may improve the hydrophilicity of the electrode, especially in the inner parts of the electrode. Moreover, the concentration of  $\text{OH}^-$  in the electrolyte is much higher than the concentration of the

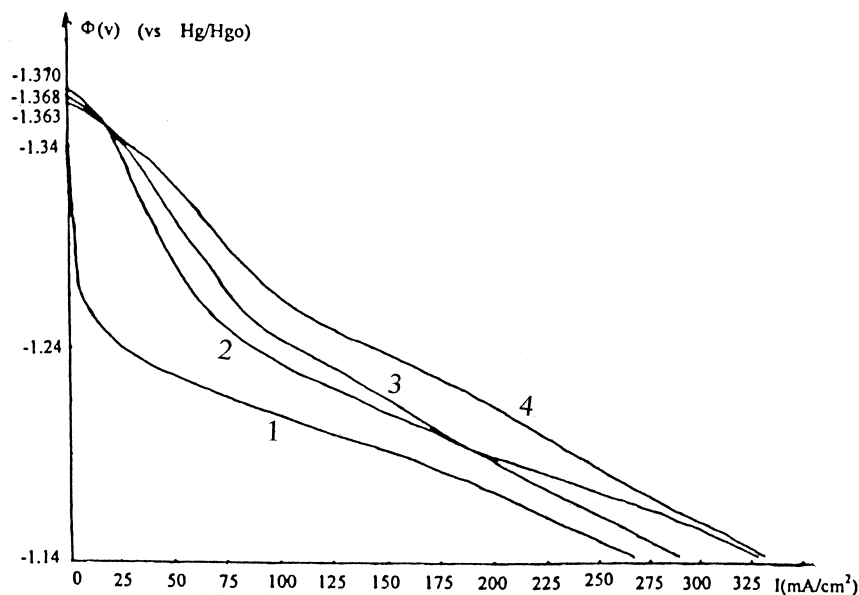


Fig. 1. Anodic polarization curves of porous zinc electrodes: (1) with no coating ('blank'); (2) coated with A ionomer film; (3) coated with B ionomer film; (4) coated with C ionomer film.

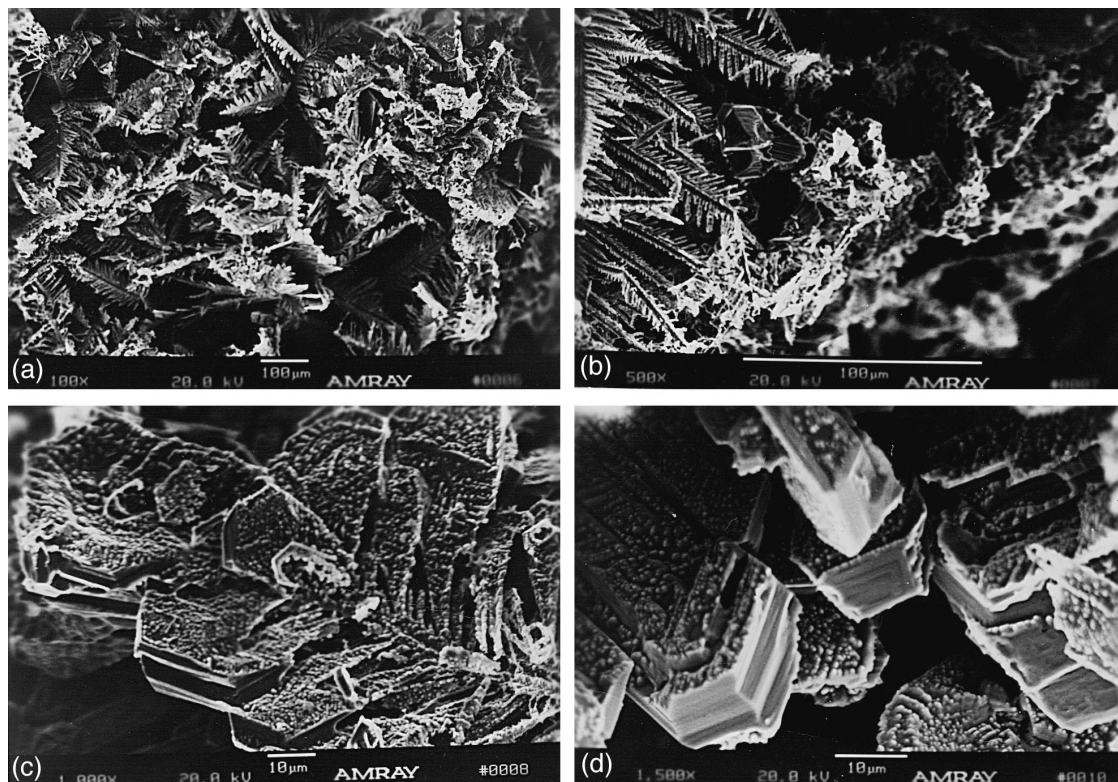


Fig. 2. Electron micrographs of a zinc electrode ('blank') after 50 discharge–charge cycles. Magnification: (a)  $\times 100$ ; (b)  $\times 500$ ; (c)  $\times 1000$ ; (d)  $\times 1500$ .

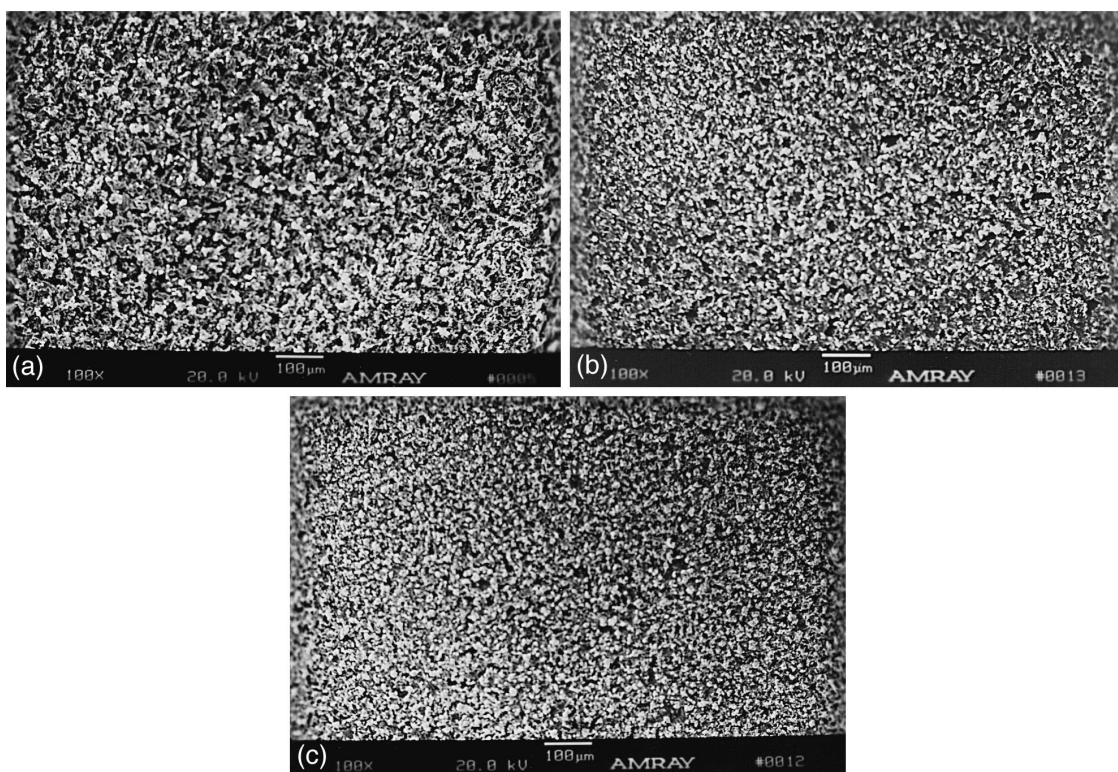


Fig. 3. Electron micrographs of zinc electrodes coated with ionomer films after 50 discharge–charge cycles. Magnification:  $\times 100$ , (a) coated with A ionomer film; (b) coated with B ionomer film; (c) coated with C ionomer film.

ionic group ( $-\text{COO}^-$ ) in the ionomer and the  $\text{OH}^-$  anions, whose ionic radius is smaller than that of the ionic microdomains of the ionomer film, can pass easily through the ionomer films under the extra electric field. That is to say, the ionomer films do not impede the passage of the ions ( $\text{OH}^-$ ) relating to the electrode reaction. Thus, the interior surface of a porous zinc electrode with an ionomer film can be fully utilized during polarization. All of these features may be responsible for the improvement in the performance of the zinc electrode.

Other anodic polarization experiments with the same porous zinc electrodes and ionomers were also carried out in 10, 20 and 40% KOH solution, respectively. The results were similar.

### 3.3. Scanning electron microscopy

Electron micrographs of zinc electrodes, 'blank' and coated with ionomer films, after 50 charge–discharge cycles (in charged state) are shown in Figs. 2 and 3, respectively.

Dendrites can be clearly seen on the uncoated ('blank') zinc electrode in Fig. 2. This indicates that the shape change of this electrode is severe. Fig. 2a–d show the morphology at different magnifications. Again, the dendritic growth can be clearly observed; large, multi-faced crystallites are revealed at a magnification of 1500 (Fig. 2d).

The morphologies of the electrodes coated with ionomers (Fig. 3a–c) are completely different from the morphology of an uncoated electrode at the same magnification (e.g., magnification  $\times 100$ ). The deposit is uniform, dense and granular, i.e., smooth rather than dendritic. The B ionomer film is found to be most effective, in producing a smooth deposit.

## 4. Conclusions

The influence of three zinc-ionomers on zinc electrodes has been studied. These ionomer films, which are in direct

contact with the electrodes, have a structure that allows ions relating to the reactions of zinc electrodes to pass through, but is impermeable to  $\text{Zn}(\text{OH})_4^{2-}$  anions which are formed during electrode discharging. Discharge experiments with constant current show that the ionomer films coated on zinc electrodes can greatly impede the elution of zinc discharge products into the electrolyte. The polarization performance of a Teflon-bonded porous zinc electrode can be greatly improved when it is coated with these zinc-ionomer films. During charge–discharge cycling, these ionomer films can reduce the dendritic growth and shape change of zinc electrodes. It is possible to synthesis the more effective ionomers used for this purpose by adjusting the contents of ionic groups and  $\text{Zn}^{2+}$  ions in the ionomers to improve the structure of the ionic microdomains.

## References

- [1] E.G. Gagnon, J. Electrochem. Soc. 133 (1986) 1989.
- [2] E.G. Gagnon, J. Electrochem. Soc. 138 (1991) 3173.
- [3] R. Jain, T.C. Adler, F.R. McLarnon, E.J. Cairns, J. Appl. Electrochem. 22 (1992) 1039.
- [4] Y. Sato, M. Kanda, H. Niki, M. Ueno, K. Murata, J. Power Sources 9 (1983) 147.
- [5] L. Binder, W. Odar, J. Power Sources 13 (1984) 9.
- [6] J. McBreen, E. Gagnon, Electrochim. Acta 26 (1981) 1439.
- [7] J. McBreen, E. Gagnon, J. Electrochem. Soc. 130 (1983) 1980.
- [8] O.C. Wagner, A. Himy, Proc. 28th Power Sources Symp., Atlantic City, (1978) 167.
- [9] R.F. Thornton, E.J. Carlson, J. Electrochem. Soc. 127 (1980) 1448.
- [10] M.A. Dzieciuch, N. Gupta, H.S. Wroblwa, J. Electrochem. Soc. 135 (1988) 2415.
- [11] T.C. Adler, F.R. McLarnon, E.J. Cairns, J. Electrochem. Soc. 140 (1993) 289.
- [12] K. Bass, P.J. Mitchell, J. Power Sources 39 (1992) 273.
- [13] G. Wilcox, P. Mitchell, J. Power Sources 28 (1989) 345.
- [14] E. Fraekowiak, M. Kiaciak, Electrochim. Acta 33 (1988) 441.
- [15] E.G. Ganon, B.S. Hill, J. Electrochem. Soc. 137 (1990) 377.
- [16] R.A. Sharma, J. Electrochem. Soc. 135 (1988) 1875.
- [17] E.G. Ganon, Y.M. Wang, J. Electrochem. Soc. 134 (1987) 2091.
- [18] J.L. Zhu, Y.H. Zhou, H.X. Yang, J. Power Sources 69 (1997) 169.
- [19] C. Li, R.A. Register, S.L. Cooper, Polymer 30 (1989) 1227.
- [20] A. Eisenberg, Macromolecules 3 (1970) 147.