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Separation and permeability of zincate ions through membranes

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Abstract

A novel method for the separation of zincate ions in alkaline media has been developed. This development uses a precipitation reaction of $Mn(OH)_2$ and application on a microporous separator (Celgarde). The amount of zinc, passed through the membranes was estimated by electrogravimetric method. Different inorganic materials in combination with the separator material have been tested. Effective low grade permeability of zincate ions and increased resistivities have been found to be related to the amount of $Mn(OH)_2$ applied on the separator.

Keywords: Separation; Permeability; Membranes; Zinc; Manganese

1. Introduction

One of the problems encountered with the use of zinc electrodes in battery systems is either the shape change due to the redistribution of the active material during cycling (the edging effect) or the solubility of the discharge products of zinc, which penetrate through the separator material and cause short-circuiting (the dendritic effect). Numerous works have been conducted to understand and /or minimize these effects and normalize the zinc electrode [1–10]. Among those measures which are mentioned in the literature and in review articles [11,12] the following steps can be categorized accordingly:

(i) additives to the electrode, e.g. HgO, PbO, $In(OH)_3$, Tl_2O_3, $Ca(OH)_2$;

(ii) additives to the electrolyte system, e.g. H_3PO_4, K_3BO_3, chromate, arsenate, fluoride;

(iii) development, improvement or additives in the separator material, e.g. polymers or polymers coated with CeO_2, $Ca(OH)_2$, $Mg(OH)_2$, $Ba(OH)_2$ and different oxides or hydroxides, and

(iv) miscellaneous measures, such as application of flowing electrolyte, auxiliary electrodes, pulse charging, stirring or vibration.

Special attention is paid to the separator method because it can be used either alone or in combination with other additives wrapped in between, thus allowing the basic functions as the electrolyte reservoir and as a barrier for the two electrode systems preventing short-circuiting. In addition to these basic advantages and requirements, a separator material should meet the following criteria for a successful operation in a battery system: (i) high ionic conductivity and low electrical resistance; (ii) availability and wider applicability; chemically resistant to the electrolyte/electrode system; (iii) non-fragility, viz. better mechanical strength, and (iv) wettability by the electrolyte.

In this study, separators combined with inorganic compounds are used in order to evaluate the permeability of zincate ions. The permeability of zinc and diffusion coefficients were then compared among the materials to establish the effectiveness towards zinc separation.

2. Experimental

The procedure used to solve the permeability of zincate ions consisted of the application of a layer of inorganic compounds, whose solubility are very low. After gelation or precipitation reactions, the products are sandwiched between two separator materials and tested in a cell compartment, see Fig. 1. Finely ground $Al(OH)_3$ with particle sizes of <38 μm was mixed with 20 wt.% Teflon, embedded in a nickel screen and sintered in air at 280 °C for evaluation and comparison with other materials. The separator material used was a commercial and battery grade Celgarde 3401 with a pore size of 0.05 μm and an electrical resistance of 0.1 Ω cm^2 at room temperature and in a 6 M KOH solution. This membrane, which is highly hydrophilic, is cut into a piece of 10 cm^2 and placed in between the electrode and the electrolyte systems.

Various inorganic compounds were tested in the cell arrangement with a couple of electrolyte compartments con-

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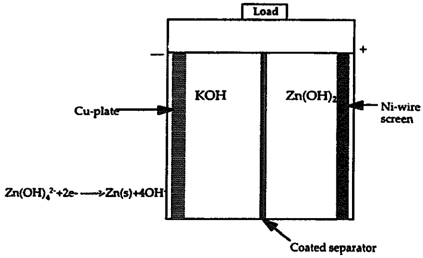

Fig. 1. Schematic of the cell configuration.

taining solutions of KOH and $Zn(OH)_2$, respectively. The permeability of zincate ions through the membrane and the deposition of zinc on the copper-plate has been assessed by applying a constant current density of 10 mA/cm^2 through the cells. This electrogravimetric method consists of electroplating of zinc onto a previously weighed copper-plate electrode and then, after the electrochemical reaction, weighing again in order to determine the amount of zinc present. An *iR* measuring instrument (Model 800, Electrosynthesis Corp., Amherst, NY) is used for evaluating the potential drop across the separator and electrolyte system. The *iR* measurement device is based on the principle of current interruption, i.e, periodical interruptions for a short time interval, usually of less than 10 μs and a rapid measurement of the resultant solution resistance across the electrodes.

3. Results and discussions

The inorganic compounds selected for the separation of zincate ions in combination with the separator materials are (i) those, whose solubility product is very low, and (ii) whose presence in the solution does not interfere or enhance the corrosion rate of zinc, i.e., excluding metals that lower the hydrogen overpotential, e.g. Fe, Ni, Co, Ge, or Sb.

The following reactions are used for the evaluation of zinc deposition on the cathode

$$2NH_4F + Ca(OH)_2 \rightarrow CaF_2 + 2NH_4OH$$
$$K_{sp}: 3.4 \times 10^{-11} \quad (1)$$

$$Mg(CH_3COO)_2 + 2KOH \rightarrow Mg(OH)_2 + 2KC_2H_3O_2$$
$$K_{sp}: 1.2 \times 10^{-11} \quad (2)$$

$$Mn(NO_3)_2 + 2NaOH \rightarrow Mn(OH)_2 + 2NaNO_3$$
$$K_{sp}: 4.0 \times 10^{-14} \quad (3)$$

where K_{sp} is the solubility constant.

Reactions (1) and (2) proceed through gelation while reaction (3) is a precipitation reaction. In reaction (3), NaOH is used instead of KOH, because the solubility of the respective salts in water are different. The colloidal particles of $Mn(OH)_2$ are then applied dropwise onto the separator, dried and then added to get several layers.

The diffusion coefficient of zincate ions through the separator and inorganic materials can be estimated by the classical method using Fick's first law

$$J = -D(\partial c/\partial x)t \quad (4)$$

where J is the instantaneous flow rate per unit area of the zincate ions across the membrane, c the concentration of zincate ions and $\partial c/\partial x$ the concentration gradient. This equation can be rewritten, simplified and be applied to the different experiments by using the following expression

$$J = -D\frac{\Delta c}{\Delta x} \quad (5)$$

$\Delta C = -8.775 \times 10^{-4}$ mol/cm^3 is the initial zinc ion concentration and corresponds to the difference between the couple of the electrolyte rooms at 0.0 and 0.8775 M; the thickness of the double-folded separator without the inorganic compounds is $\Delta x = 5 \times 10^{-3}$ cm. The flux J can be calculated from the tabulated values of the zinc permeability given in Table 1.

Both CaF_2 and $Mg(OH)_2$ gels tend to swell in the separators; this may lead to a cracking of the material or the separator in the cell system. Thus, additional work is done to optimise $Mn(OH)_2$ in order to decrease its high electrical resistance. Different layers of $Mn(OH)_2$ (weights) are coated on one or both separator materials; the results are given in Fig. 2 as a function of both the resistance (Ω cm^2) and the

Table 1
Comparison of the tests

Type	Zn permeability (mg/h)	J (10^{-6} mol cm^{-2} h^{-1})	D (10^{-8} cm^2 s^{-1})
Two separators	28.46	43.5	6.89
$Al(OH)_3$ + Teflon	5.0	7.65	8.47
CaF_2	3.66	5.6	1.775
$Mg(OH)_2$	0.07	0.11	0.051
$Mn(OH)_2$	0.03	0.05	0.006

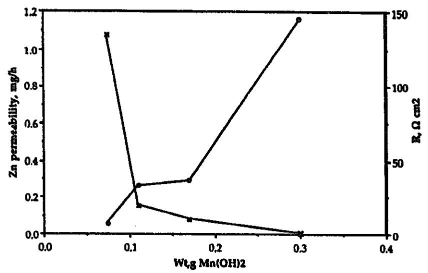

Fig. 2. Amount of $Mn(OH)_2$ coated on the separator as function of zinc permeability and resistance.

zinc permeability (mg/h). The results show that the two blank separator materials (Celgarde) have the highest zinc permeability and lowest resistance, followed by $Al(OH)_3$ blended with Teflon. The increase in resistance versus $Mn(OH)_2$ (weight) is due to the plugging of the pores of the membrane by the very fine colloidal particles and increasing layers of the material.

4. Conclusions

$Mn(OH)_2$ in combination with the organic membrane gives a higher and effective zincate ion separation capacity, where almost total separation was possible.

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