JOURNAL OF APPLIED ELECTROCHEMISTRY 3 (1973) 99–102

Cathodic polarization characteristics of poly (4-vinylpyridine) bromine complex

T. SAITO*, H. IKEDA*, Y. MATSUDA† AND H. TAMURA

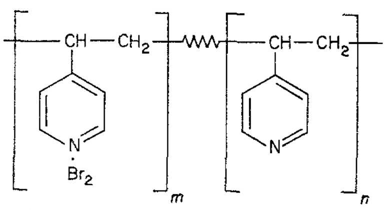
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Osaka, Japan

Received 31 July 1972

The cathodic polarization characteristics of the electrode consisting of poly (4-vinylpyridine) bromine complex and graphite powder were investigated. The electrolyte was propylene carbonate containing 1 M LiBr. The rest potential of the electrode was approx. 0·5 V (versus SCE). The coulometric efficiency of the continuous discharge was 52–53%.

1. Introduction

In the course of the investigation and the development of batteries whose electrolytes are non-aqueous organic solvents, various transition metal halides [1–6], oxides [1, 7, 8] and sulfides [9, 10] have been used as cathode materials. However, some organic compounds which can be used as cathodes have recently been introduced in place of the materials cited above. The possibility of using these organic cathode materials was referred to by Jasinski [11]. Dichloroisocyanuric acid [12], pyridine-hydrobromide-perbromide [13] and pyridine-hydroiodide-periodide [13] have been used for the cathodes of batteries with Li anodes and non-aqueous organic electrolytes. In this work, poly (4-vinylpyridine) bromine complex, was investigated as a cathode material, because its solubility is low in propylene carbonate and the bromine complex is easily prepared by the reaction with bromine. The discharge characteristics of a cathode consisting of poly (4-vinylpyridine) bromine complex and the conditions for the preparation of this cathode have been investigated.



2. Experimental technique

The construction of the electrolytic cell is shown in Fig. 1. The test electrode was a pellet which was prepared by pressing the mixture of the poly vinylpyridine bromine complex and graphite

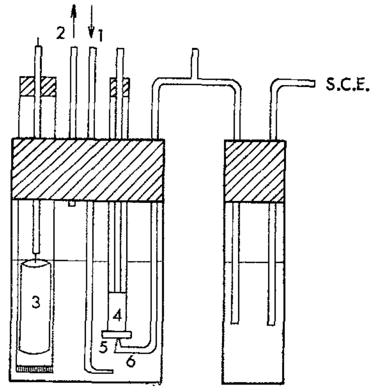


Fig. 1. Electrolytic cell. 1, dry nitrogen inlet; 2, dry nitrogen outlet; 3, counter electrode; 4, graphite lead; 5, test electrode; 6, luggin capillary.

---

* Present address: Research and Development Center, Sanyo Electric Co. Ltd., Osaka, Japan.

† Present address: Department of Industrial Chemistry, Faculty of Engineering, Yamaguchi University, Tokiwadai, Ube, Yamaguchi, Japan.

powder (passed through a sieve of 145 mesh; commercial product by Kishida Chemicals, Ltd.). The surface area of this electrode was 1·33 cm^2 and the weight was 0·5 g. The pellet electrode was mounted at the bottom of a glass tube with epoxy resin, and graphite powder and a carbon rod were used to make electrical contact. The counter electrode was a Pt cylinder having a large surface area and it was positioned in a glass tube closed at the bottom with a sintered glass diaphragm. The reference electrode was a saturated calomel electrode which was connected with the cell through a Luggin capillary, intermediate solution and agar-agar bridge. The electrolyte solution was propylene carbonate containing 1 M LiBr. The oxygen in the electrolyte was removed by bubbling dry nitrogen gas through the solution.

The procedure for the preparation of poly (4-vinylpyridine) bromine complex, the cathodic active material, is as follows. The 4-vinylpyridine in 30 wt % aqueous solution was polymerized at 50°C for 20 h, with nitrogen bubbling through it. The polymer obtained was a brown gummy material. This was washed in boiling water, dissolved in tert.-butanol and precipitated with benzene. The precipitate was dried at 60°C under reduced pressure after filtration. The mean molecular weight was approximately 10 000 by the VPO method with $CHCl_3$. Then, by addition of a solution of bromine in methanol to the methanolic solution of 2 wt % vinylpyridine polymer, red crystals of the bromine complex of the polymer were precipitated. These were filtered and dried. The ratio of bromine molecules to nitrogen atoms was 0·22 in the poly (4-vinylpyridine) bromine complex.

Propylene carbonate was obtained through distillation of the commercial material (Extra Pure Reagent by Nakarai Chemicals, Ltd.) under a reduced pressure of 3–4 mm Hg at 85°C; its H_2O content was 30 ppm. Lithium bromide (JIS Guaranteed Reagent) was used after drying at 250°C for 10 h.

The measurements of polarization were made under stationary state conditions by using a potentiostat and the continuous discharging curves were obtained by using a constant d.c. source and a recorder. The temperature of the electrolytic cell was controlled with a thermostat.

3. Results and Discussion

The effect of the weight ratio of poly (4-vinylpyridine) bromine complex to graphite powder in the cathode on the cathodic polarization characteristics is shown in Fig. 2. In this case, the forming pressure was 2 t cm^{-2} for the preparation of the pellet electrode. The open circuit voltages were about 0·5 V against SCE. The results showed that the polarization was the least in the case of the cathode consisting of 80% of the polymer and 20% of graphite powder. As to the cathode consisting of 90% of the polymer and 10% of graphite powder, the polarization was so large that the limiting current was lower than 0·1 mA (for an electrode with a surface area 1·33 cm^2) owing to the increase in resistance.

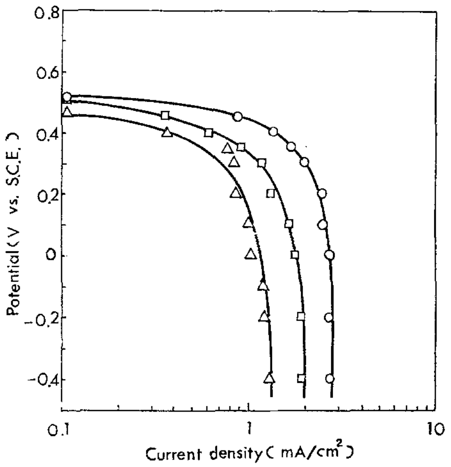


Fig. 2. Potential-current density curves in 1 M LiBr-PC at 30°C, 2t cm^{-2}; ○, polymer 80%, graphite 20%; □, polymer 70%, graphite 30%; △, polymer 50%, graphite 50%.

Fig. 3 shows the relation between the forming pressure in the preparation of the electrode and the cathodic polarization. The composition of the cathode was 80% of the polymer and 20% of the graphite powder. The pressure was 1 t cm^{-2}, 2 t cm^{-2} and 3 t cm^{-2}. The influence of the forming pressure was small, although the electrode prepared by applying 2 t cm^{-2} showed the best polarization characteristics.

Batteries with non-aqueous electrolyte are usually operative at low temperature. The influence of temperature on the cathodic performance of the electrode is shown in Fig. 4. The cathodic performance was still acceptable at −4°C, but the electrode was less polarized at higher temperatures.

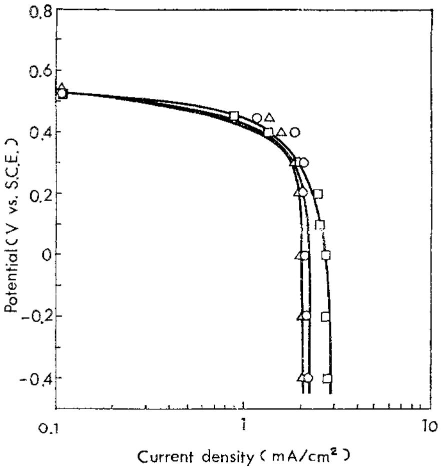


Fig. 3. Potential-current density curves in 1 M LiBr-PC at 30°C, polymer 80%, graphite 20%; ○, 1t cm^{-2}; □, 2t cm^{-2}; △, 3t cm^{-2}.

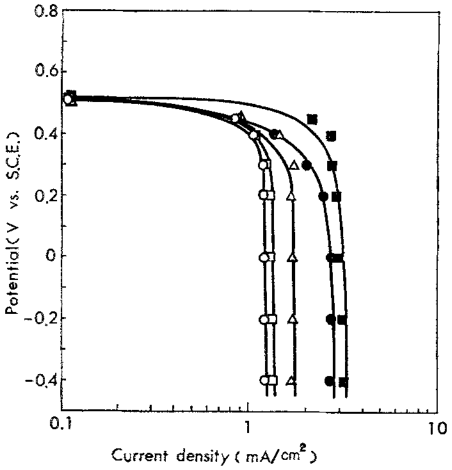


Fig. 4. Potential-current density curves in 1 M LiBr-PC, polymer 80%, graphite 20%, 2t cm^{-2}; ○, −4°C; □, 5°C; △, 15°C; ●, 30°C; ■, 40°C.

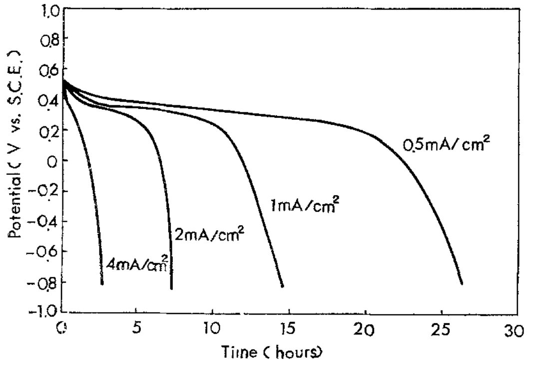
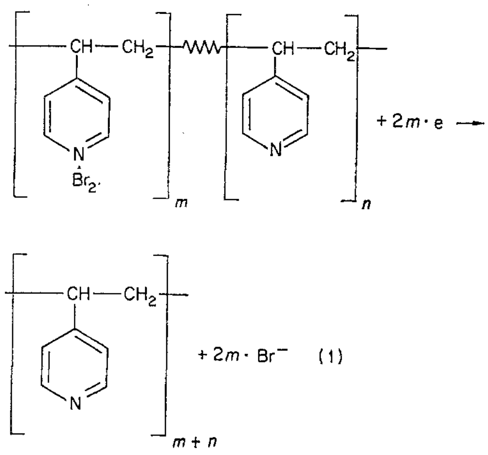


Fig. 5. Discharge curves in 1 M LiBr-PC at 30°C, polymer 80%, graphite 20%, 2t cm^{-2}.

The results of the discharge at constant current densities are shown in Fig. 5. The composition of the electrode was 80% of the polymer and 20% of graphite powder, and the forming pressure was 2 t cm^{-2}. At lower discharge current density, a substantially steady discharge was observed. The coulometric efficiencies of poly (4-vinylpyridine) bromine complex were 52–53% by assuming that one molecule of bromine in the cathode discharged in the two electron system as shown in Equation (1).



The cathode material itself, poly (4-vinylpyridine) bromine complex, was insoluble in the electrolyte, but approximately 22% of the bromine from the cathode was released into the electrolyte without discharge. The capacity of the electrode would be enhanced by increasing the content of bromine in the electrode although a suitable method for adding the bromine would have to be found.

References

[1] R. Jasinski, *Electrochem. Technol.*, **6** (1968) 28.
[2] M. Eisenberg and K. Wong, Proc. 23rd Annual Power Source Conf., p. 74 (1969).
[3] C. Pistoia, *J. Electrochem. Soc.*, **118** (1971) 153.
[4] C. C. Liang and P. Bro, *J. Electrochem. Soc.*, **116** (1969) 1322.
[5] M. Shaw and R. Chand, Proc. 23rd Annual Power Source Conf. p. 76 (1969).
[6] M. M. Nicholson, Proc. 24th Power Source Symposium, p. 101 (1970).

[7] R. Jasinski, *J. Electroanal. Chem.*, **26** (1970) 189.
[8] L. Campanella and G. Pistoia, *J. Electrochem. Soc.*, **118** (1971) 1905.
[9] J. P. Gabano, G. Gerbier and J. F. Laurent, Proc. 23rd Annual Power Source conf., p. 80 (1969).
[10] R. Jasinski and B. Burrows, *J. Electrochem. Soc.* **116** (1969) 423.
[11] R. Jasinski, 'High-Energy Batteries', Plenum Press, New York (1967).
[12] D. L. Williams, J. J. Byrne and J. S. Driscoll, *J. Electrochem. Soc.*, **116** (1969) 2.
[13] Y. Matsuda, T. Inoue, H. Yoneyama and H. Tamura, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Soc.*), 74 (1971) 2205.