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TECHNICAL NOTE

The properties of some mixed organic electrolyte solutions and their effects on the anodic performances of Mg electrodes

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In the course of the studies on high energy batteries with organic electrolytes, Li has generally been used as the anode, but sometimes Al [1, 2], Mg [1] and Be [3] have been employed. With regard to the electrolyte, the influences of the dielectric constants and viscosities of the organic solvents on the anodic polarization characteristics of Al electrodes have recently been reported by Matsuda *et al.* [2]. Some other workers [4-6] have observed the effect of mixing organic electrolytes on the conductivities. In the present study the properties of electrolyte solutions composed of mixed organic solvents with perchlorates and the polarization characteristics of Mg anodes in these solutions were investigated.

Formamide (FA), acetonitrile (AN) and propylene carbonate (PC) were purified by the methods described in a previous report [2]. Tetrahydrofurane (THF) and 1, 2-dimethoxyethane (1, 2-DME) were dehydrated with Na and then distilled. The final water contents were 70 ppm in PC, 200 ppm in THF, 490 ppm in 1, 2-DME and 200 ppm in AN, respectively. Sodium perchlorate and lithium perchlorate were used after drying under reduced pressure at 100 and 160°C for 10 h, respectively.

The viscosities of the solvents were measured with an Ostwald viscometer and the dielectric constant was measured by means of the resonance method with a dielectric analyser. The electrical conductivity of the electrolyte was measured with an impedance bridge using 1 kHz AC. The electrolytic cell used was a 50 ml beaker. The test electrode was a Mg plate (1 × 1 × 0.2 cm) containing 3 wt.% Al and 1 wt.% Zn, fixed at the edge of a glass tube with epoxy resin. It was polished with emery paper (No. 1000). The electric lead was a Cu wire which was connected to the test electrode with silver paste. The counter electrode was a Pt plate with large surface area and the reference electrode a S.C.E. which was connected to a Luggin capillary through a salt bridge. In the polarization measurements, the current was measured 3 min after applying the potential. Purified N_2 gas was continuously bubbled through the electrolyte solution.

Some physical properties of the pure solvents are shown in Table 1, and the measured values of density and viscosity of the solutions containing sodium perchlorate or lithium perchlorate are presented in Table 2. According to theory, the higher the dielectric constant and the lower the viscosity of a solvent, then the higher is the conductivity of the solution. In further experiments, the properties of mixed solvents with and without perchlorates were determined. The performances of Mg anodes in these solutions were also investigated.

Tables 3 and 4 show some properties of the mixed solvents (vol. 1:1) with and without perchlorates. The physical properties of the mixed solvents were generally intermediate in value between those of the two pure solvents. The conductivities of some mixed organic solvents based on FA

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Table 1. Some physical properties of organic solvents, 25° C

Solvent	*Density* (g cm³)	*Viscosity* (cp)	*Dielectric constant*	*Reference*
FA	1.13	3.30	111.0*	7
1, 2-DME	0.86	0.46	7.20	7
THF	0.89	0.40	7.58	7
AN	0.78	0.33†	37.5*	7
PC	1.2	2.5	65	8

* 20° C.
† 30° C.

Table 2. Density and viscosity of organic solvents containing perchlorates, 25° C

Electrolyte	*Density* (g cm³)	*Viscosity* (cp)
FA cont. 1 M $NaClO_4$	1.19	5.33
1, 2-DME cont. 1 M $NaClO_4$	0.96	0.97
THF cont. 1 M $NaClO_4$	0.97	0.96
AN cont. 1 M $NaClO_4$	0.87	0.68
1, 2-DME cont. $LiClO_4$	–*	–*
THF cont. 1 M $LiClO_4$	0.96	0.96
PC cont. 1 M $LiClO_4$	1.26	8.80

* Slightly soluble.

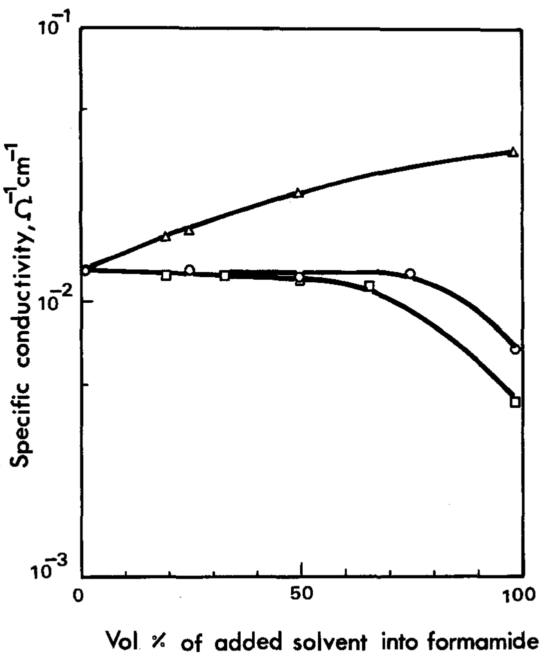

Fig. 1. Specific conductivities of the electrolyte solutions [1]. ○, FA + 1, 2-DME containing 1 M $NaClO_4$; □, FA + THF containing 1 M $NaClO_4$; △, FA + AN containing 1 M $NaClO_4$; 25° C.

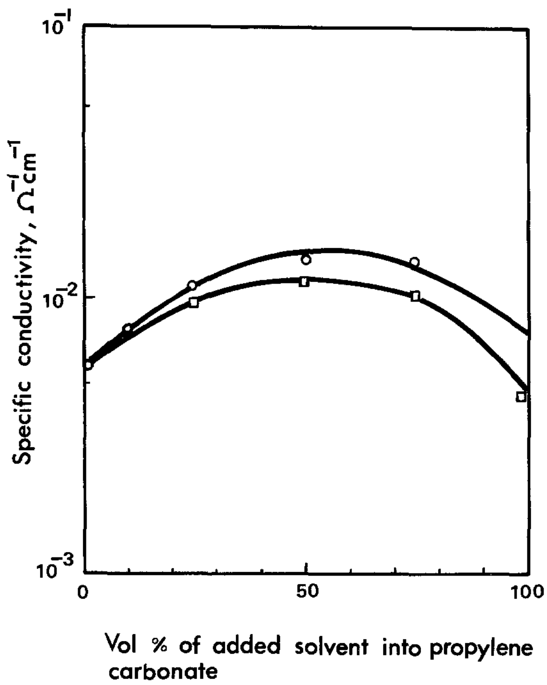

Fig. 2. Specific conductivities of the electrolyte solutions [2]. ○, PC + 1, 2-DME containing 1 M $LiClO_4$; □, PC + THF containing 1 M $LiClO_4$; 25° C.

containing 1 M sodium perchlorate as a function of the vol % were measured,; the results are shown in Fig. 1. Fig. 1. shows that the conductivity of the FA–AN system is increased by the addition of AN, but that of the FA–THF and 1, 2-DME systems is constant in the range of 100 to ca. 30 vol % AN and decreases in the range below ca. 30 vol %. For the FA–AN system, the high conductivity shown in Fig. 1 is probably related to the high dielectric constant and low viscosity values (Table 3). Similar diagrams of the mixed solvents based on PC containing 1 M lithium perchlorate are shown in Fig. 2.

The cathodic polarization curves of Mg electrodes in various organic electrolytes are shown in Fig. 3.

Table 3. Some physical properties of mixed organic solvents (vol. 1:1), 25°C

Solvent	*Density* ($g\,cm^{-3}$)	*Viscosity* (cp)	*Dielectric constant*
FA + 1, 2-DME	1.01	2.10	59.8
FA + THF	1.01	1.96	56.5
FA + AN	0.96	1.11	72.4
PC + 1, 2-DME	1.04	1.02	52.5
PC + THF	1.04	0.99	52.1

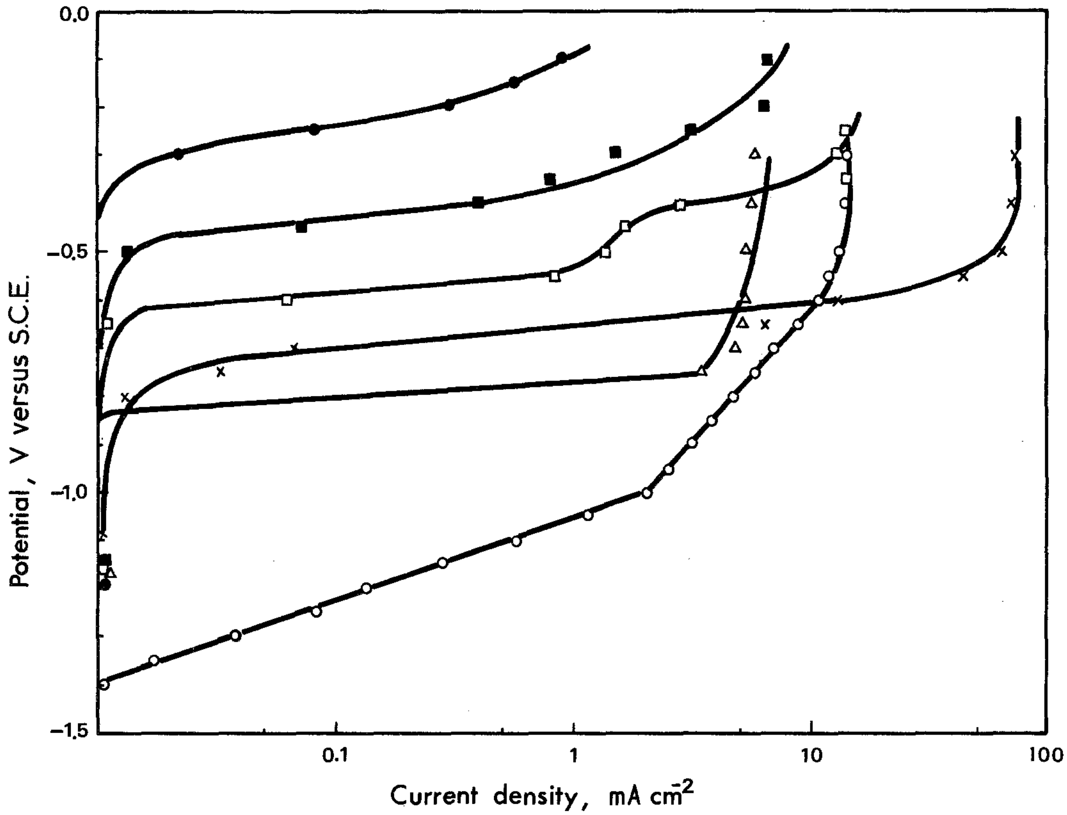

Fig. 3. Anodic polarization characteristics of Mg electrodes in various electrolyte solutions [1]. ○, FA containing 1 M $NaClO_4$; □, 1, 2-DME containing 1 M $NaClO_4$; X, AN containing 1 M $NaClO_4$; ●, PC containing 1 M $LiClO_4$; ■, THF containing 1 M $LiClO_4$; 25°C.

Table 4. Density and viscosity of mixed organic solvents (vol. 1:1) containing perchlorates, 25°C

Electrolyte	*Density* ($g\,cm^{-3}$)	*Viscosity* (cp)
FA + 1, 2-DME cont. 1 M $NaClO_4$	1.09	4.36
FA + THF cont. 1 M $NaClO_4$	1.09	3.80
FA + AN cont. 1 M $NaClO_4$	1.04	1.84
PC + 1, 2-DME cont. 1 M $LiClO_4$	1.12	2.36
PC + THF cont. 1 M $LiClO_4$	1.12	2.62

In Fig. 3, the rest potential was lowest in FA containing 1 M sodium perchlorate and the polarization relatively small. In the other electrolyte solutions, the rest potentials of the Mg electrode were higher than that in FA. The electrode potentials rose rapidly at low currents and thin black films were observed on the surfaces of the test electrodes. At higher potentials these films disappeared. However this black film was not observed at all on the Mg electrode in FA.

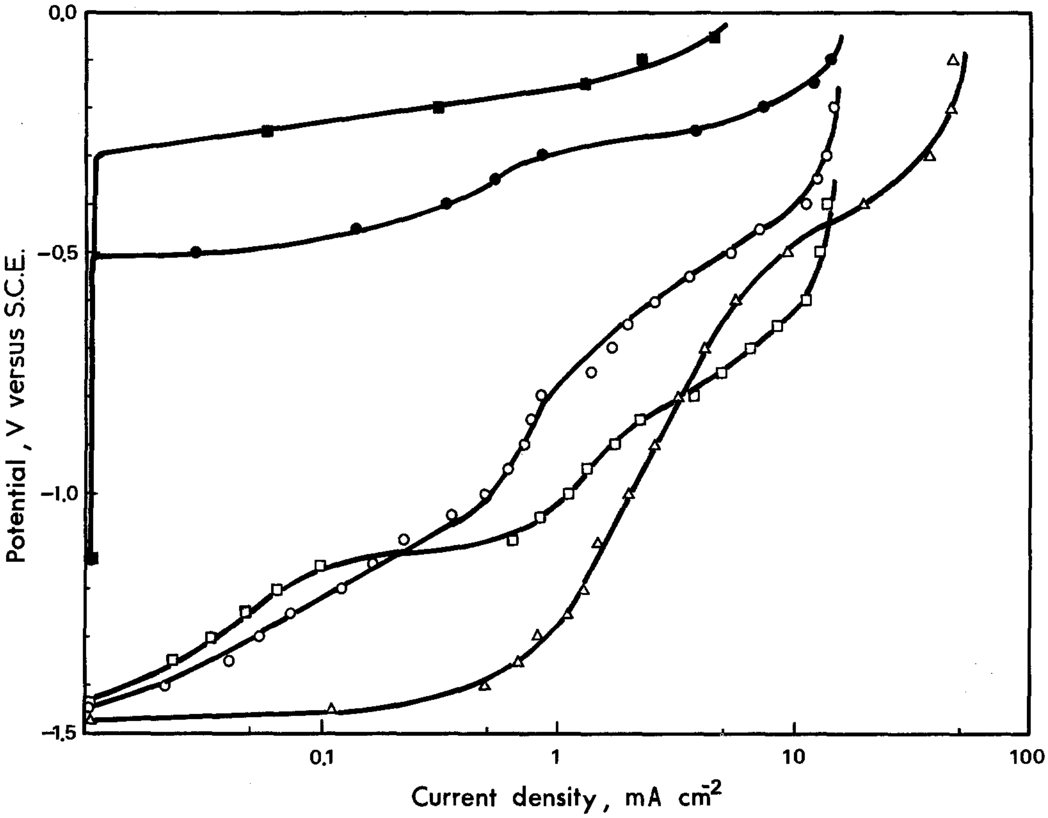

Fig. 4. Anodic polarization characteristics of Mg electrodes in various electrolyte solutions [2]. ○, FA + 1, 2-DME (vol. 1:1) containing 1 M $NaClO_4$; □, FA + THF (vol. 1:1) containing 1 M $NaClO_4$; △, FA + AN (vol. 1:1) containing 1 M $NaClO_4$; ●, PC + 1, 2-DME (vol. 1:1) containing 1 M $LiClO_4$; ■, PC + THF (vol. 1:1) containing 1 M $LiClO_4$; 25°C.

Polarization curves in some mixed solvents (vol. 1:1) are shown in Fig. 4. These polarization curves were somewhat unstable, but the reason for this could not be ascertained. In the FA-1, 2-DME, FA–THF and FA–AN systems, the rest potentials were in the range of −1.4 to −1.5 V versus S.C.E. The performance of the Mg anode was improved by the addition of FA. A similar improvement was not observed in the mixed PC systems containing 1 M lithium perchlorate.

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