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Conductivity of low-temperature electrolytes for magnesium batteries

Gopu Kumar, Subramanyan Vasudevan and Natchi Muniyandi
Central Electrochemical Research Institute (CSIR), Karaikudi–623 006 (India)

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Abstract

Specific conductivities have been determined for $MgCl_2$, $MgBr_2$, $Mg(ClO_4)_2$, 2 M $Mg(ClO_4)_2+x$ M $MgCl_2$, and 2 M $Mg(ClO_4)_2+x$ M $MgBr_2$ (where $x=0.1$ to 2 M) in pure water over the concentration range 0.1 to 3 M at +20, +10, 0, −10 and −20 °C. The conductivities increase in the order $MgBr_2 > MgCl_2 > Mg(ClO_4)_2$. Conductance maxima have been evaluated and the values of the 'a' and 'b' constants of Casteel-Amis equation have been obtained. A comparative study with the available literature data for $MgCl_2$ has been undertaken. Cells comprising Mg/electrolyte/*m*-dinitrobenzene (1 V; 3 A h) have been fabricated and tested at +20 and −20 °C using the maximum conductivity of the different electrolytes. Mixed electrolytes have also been investigated. From the observed discharge behaviour, 2.0 M $Mg(ClO_4)_2$ appears to be the most promising electrolyte solution for practical magnesium batteries that are required to operate over a wide temperature range.

Introduction

Data on the transport properties of electrolytes (viz., conductivity, viscosity, dielectric constant, etc.) are required for the development of battery systems [1–5]. While there have been many studies (e.g., refs. 6–9) on dilute solutions, data on concentrated solutions are scant [10]. Recently, some investigations have been reported on the conductivity of concentrated solutions of magnesium chloride and sulfate in both aqueous and mixed solvents [11]. Since the data exhibited slight discrepancies, a study has been made here of the conductance of aqueous solutions of magnesium halide, perhalates, and their mixtures over wide ranges of temperature and concentration.

In addition to the positive and negative electrodes, the electrolyte is a major determinant of battery performance. For low-temperature operation, the freezing point of the electrolyte, as well as the solution conductivity and compatibility with the electrode materials, are responsible for the performance of a battery.

In this communication, a report is given of the conductivity data for aqueous solutions of $MgCl_2$, $MgBr_2$, $Mg(ClO_4)_2$, 2 M Mg $(ClO_4)_2+x$ M $MgCl_2$ and 2 M $Mg(ClO_4)_2+x$ M $MgBr_2$ at +20 to −20 °C over the concentration range 0.1 to 3 M. The objective of the work is to obtain information that is presently unavailable, but is necessary for the development of a suitable electrolyte solution for magnesium batteries that are required to operate over a wide range of temperatures.

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Experimental

Electrolyte preparation

Magnesium chloride, magnesium bromide (LOBA/Chemie, AR) and magnesium perchlorate (Merck, AR, Germany) were purified. Conductivity water was prepared by redistilling triple-distilled water over potassium permanganate in an all-glass unit. The specific conductance of the water ranged from 2 to 3×10^{-6} mho. Freshly-prepared water was used in the preparation of all the solutions. Weight and vacuum corrections were made for all solutions.

Cell construction

Magnesium alloy sheets (AZ 31] of dimensions $4\times6\times0.5$ cm were used as the anode and a copper grid of the same dimensions as current-collector for the cathode.

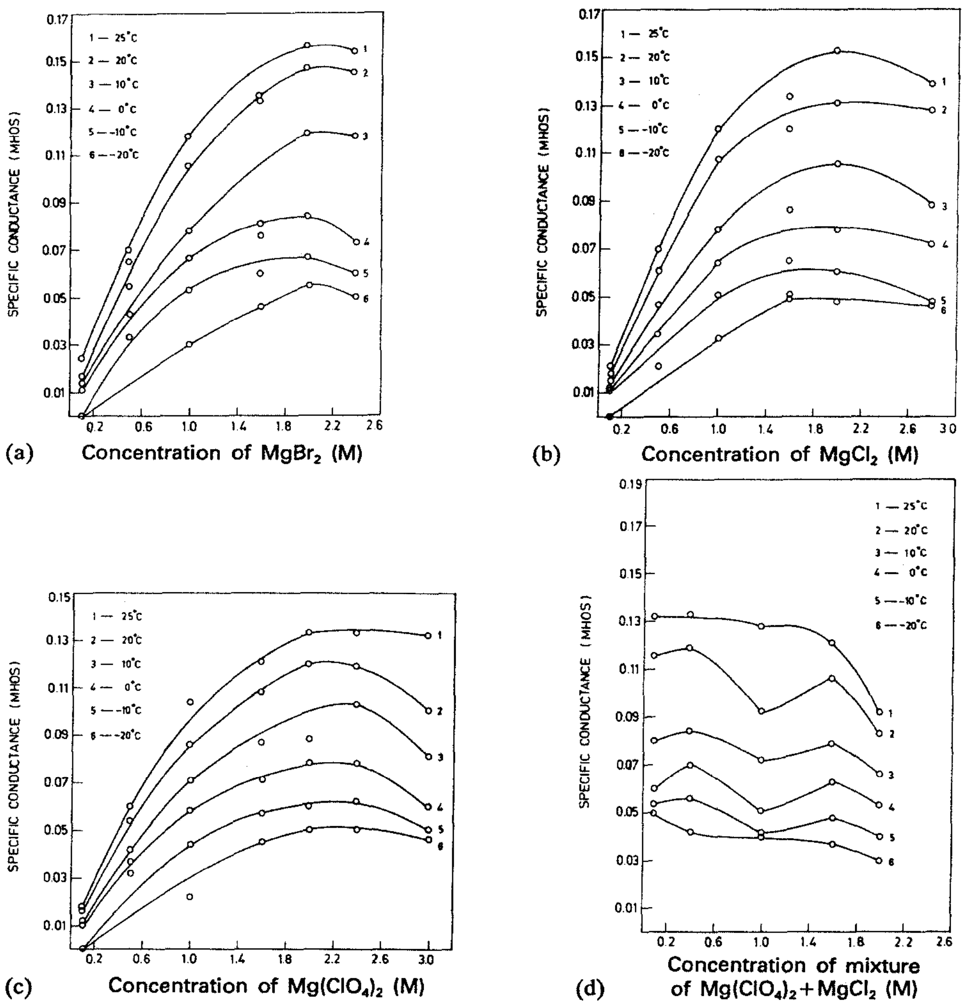
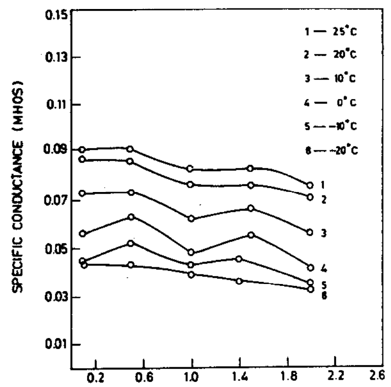


Fig. 1. *(continued)*



(e) Concentration of mixture of $Mg(ClO_4)_2+MgBr_2$ (M)

Fig. 1. Variation of specific conductance with concentration at different temperatures: (a) magnesium bromide; (b) magnesium chloride; (c) magnesium perchlorate; (d) mixture of magnesium perchlorate (2.5 M) and magnesium chloride; (e) mixture of magnesium perchlorate (2.5 M) and magnesium bromide.

The latter was prepared using 3 g *m*-dinitrobenzene, 40 to 50 wt.% acetylene black, and an aqueous solution of a binder (e.g., carboxymethylcellulose, polyvinylalcohol, teflon, etc.). This mixture was pressed on a copper grid at an optimized pressure. The cathode was placed between two anodes using a cellophane separator. The electrode packs were loosely bound with nylon thread and placed in a suitable container that contained the test electrolytes. The cells were immersed in a constant-temperature bath in order to maintain the required test temperature. Finally, the cells were discharged at either a 100 or a 200 mA current drain.

Test method

Conductance measurements were made by means of Wayne-Kerr autobalance precision bridge (B 331/MK 11) with an accuracy of $\pm 0.01\%$. A frequency of $\omega = 10^4$ rad s^{-1} was employed with a standard dip-type conductivity cell. The cell constant was 0.796 cm^{-1}. The conductivity cell was standardized using 0.1 and 0.01 D KCl solutions and agreed well with the literature values.

Results and discussion

Specific conductance data for $MgCl_2$, $MgBr_2$, $Mg(ClO_4)_2$, 2 M $Mg(ClO_4)_2+x$ M $MgCl_2$ and 2 M $Mg(ClO_4)_2+x$ M $MgBr_2$ in pure water at +20, +10, 0, −10 and −20 °C in the concentration range 0.1 to 3 M are presented in Fig. 1. It is interesting to note that a well-defined maximum exists for all the electrolytes investigated at all temperatures above −10 °C. Such conductance maxima at 25 °C have also been observed by other workers [12–16] for other unsymmetrical electrolytes such as $CaCl_2$, $NiCl_2$, $CoCl_2$, $CdCl_2$ and $ZnCl_2$ which are summarized in Table 1. The existence of such maxima does not indicate [17] the presence of ion associates either unless it occurs at low concentration or the conductance at the maximum is low. The conductance maxima are generally attributed to the opposing effects of the increase in salt concentration, thereby decreasing the ionic mobility. In the case of higher concentrations,

TABLE 1

Maximum of specific conductance in aqueous solutions of various 2:1 electrolytes at 25 °C

Electrolyte	K_{max} (Ω^{-1} cm^{-1})	C_{max} (M)
$CaCl_2$	0.20	2.5
$NiCl_2$	0.33	2.3
$CoCl_2$	0.14	2.1
$CdCl_2$	0.028	1.0
$ZnCl_2$	0.105	2.5

TABLE 2

Comparison of molar conductivity values for $MgCl_2$ at 25 °C

Concentration (M)	Λ_m (S cm^2 mol^{-1})		
	Present work	Phang *et al.* [14]	Weingartener *et al.* [10]
0.5	140	140	142.60
1.0	120	118	117.50
1.5	89.3	94.74	96.43
2.0	76.5	72	78.65
2.7	51.5	53	58.55

TABLE 3

Comparison of various parameters of Casteel-Amis equation for $MgCl_2$ at 25 °C

	μ	K_{max}	a	b
Casteel-Amis [11]	2.0434	0.16033	0.67797	−0.14941
Present work	2.0	0.153	0.72	−0.141

the decrease in ionic mobility dominates over the ionic concentration and therefore the conductivity decreases. Hence, a maximum in conductance is observed at a particular combination of salt/solvent/temperature. Barthel [2] suggested that the conductance maximum is due to the increase in the number of ion pairs, and higher clusters, before the solubility limit is reached. It is interesting to note [18] that in the case of $MgCl_2$ and $Mg(ClO_4)_2$ in non-aqueous solvents acetonitrile, propylene carbonate, dimethylformamide, γ-butyrolacetone) similar maxima are observed, but at lower salt concentrations. This suggests the development of extensive ion association.

A comparison of results obtained for $MgCl_2$ at 25 °C with those reported previously [10, 11, 14] are presented in Tables 2 and 3. The values of molar and equivalent conductivities in the case of $MgCl_2$, $MgBr_2$ and $Mg(ClO_4)_2$, different temperatures are presented in Tables 4 to 6, respectively. The data in Table 2 show that the values of molar conductivities for $MgCl_2$ are in good agreement for solutions above 0.5 M.

TABLE 4

Molar (Λ_m) and equivalent (Λ_e) conductivities of $MgCl_2$ at various temperatures and concentrations

Concentration (M)	Temperature (°C)									
	+20		+10		0		−10		−20	
	Λ_m	Λ_e	Λ_m	Λ_e	Λ_m	Λ_e	Λ_m	Λ_e	Λ_m	Λ_e
0.1	180	90	150	75	120	60	110	55		
0.5	122	61	94	47	68	34	42	21		
1.0	107	54	78	39	64	32	51	26	33	17
1.5	80	40	57	27	43	22	34	17	33	16
2.0	66	33	53	27	39	20	31	15	24	12
2.7	47	24	33	16	27	13	18	9	17	9

TABLE 5

Molar (Λ_m) and equivalent (Λ_e) conductivities of $MgBr_2$ at various temperatures and concentrations

Concentration (M)	Temperatures (°C)									
	+20		+10		0		−10		−20	
	Λ_m	Λ_e	Λ_m	Λ_e	Λ_m	Λ_e	Λ_m	Λ_e	Λ_m	Λ_e
0.1	170	85	140	70	110	55				
0.5	130	65	110	55	86	43	66	33		
1.0	105	53	78	39	67	34	53	27	30	15
1.5	89	44	54	27	51	25	40	20	31	15
2.0	74	37	60	30	42	21	34	17	28	14
2.5	58	29	47	24	29	15	24	12	20	10

TABLE 6

Molar (Λ_m) and equivalent (Λ_e) conductivities of $Mg(ClO_4)_2$ at various temperatures and concentrations

Concentration (M)	Temperature (°C)									
	+20		+10		0		−10		−20	
	Λ_m	Λ_e	Λ_m	Λ_e	Λ_m	Λ_e	Λ_m	Λ_e	Λ_m	Λ_e
0.1	160	80	120	60	100	50				
0.5	108	54	84	42	74	37	64	32		
1.0	86	43	71	33	58	29	44	22	22	11
1.5	72	36	58	29	47	24	38	19	30	15
2.0	60	30	44	22	34	17	28	14	25	13
2.5	48	24	41	21	31	16	25	12	20	10
3.0	33	17	27	14	20	10	17	8	15	8

TABLE 7

Values of parameters of Casteel-Amis equation for various electrolytes at different temperatures

Electrolyte	Temperature (°C)	a	b	μ	K_{max}
$MgBr_2$	20	0.82	−0.130	2.0	0.147
	10	0.88	−0.091	2.0	0.119
	0	0.94	−0.032	2.0	0.084
$MgCl_2$	20	0.79	−0.130	2.0	0.131
	10	0.66	−0.169	2.0	0.105
	0	0.52	−0.222	2.0	0.078
$Mg(ClO_4)_2$	20	0.72	−0.149	2.0	0.120
	10	0.74	−0.112	2.5	0.103
	0	0.76	−0.072	2.5	0.078

TABLE 8

Capacity (A h) of Mg/electrolyte/*m*-dinitrobenzene cell in different electrolytes[a]

Electrolyte	Temperature (°C)	Capacity (A h)	
		100 mA drain	200 mA drain
$MgCl_2$	+25	2.50	1.70
	−20	0.73 (29%)	0.34 (20%)
$MgBr_2$	+25	2.10	1.50
	−20	0.53 (30%)	0.30 (20%)
$Mg(ClO_4)_2$	+25	2.80	1.80
	−20	0.84 (30%)	0.36 (20%)
2 M $Mg(ClO_4)_2$	+25	2.40	1.50
+0.5 M $MgCl_2$	−20	0.60 (25%)	0.27 (18%)
2 M $Mg(ClO_4)_2$	+25	2.30	1.30
+0.5 M $MgBr_2$	−20	0.58 (25%)	0.22 (17%)

[a]Values in parentheses represent the percentage capacity with respect to room temperature.

Furthermore, excellent agreement (Table 3) is observed with the original data of Casteel and Amis [11] for $MgCl_2$ at 25 °C.

Conductance data at higher concentration can be represented by the empirical Casteel-Amis equation [11]:

$$\frac{K}{K_{max}} = \left(\frac{m}{\mu}\right)^a \exp\left[b(m-\mu)^2 - \frac{a}{\mu}(m-\mu)\right] \qquad (1)$$

where: K and K_{max} are specific conductance and maximum specific conductance at concentration m and μ; respectively; a and b are empirical constants. The values of a, b, and K_{max} for $MgCl_2$, $MgBr_2$ and $Mg(ClO_4)_2$ at different temperatures are presented in Table 7.

Based on the above conductivity studies, and in order to arrive at a practical electrolyte solution for magnesium batteries, small-capacity magnesium/*m*-dinitrobenzene cells were fabricated using different electrolytes of maximum conductivity (Table 7). The performance characteristics of these cells were evaluated at +25 and −20 °C and the discharge behaviour is presented in Table 8. It is surprising to note that the capacity of the cells using a $Mg(ClO_4)_2$ electrolyte is maximum. The capacity decreases in the sequence: $Mg(ClO_4)_2 > MgCl_2 > MgBr_2 > 2$ M $Mg(ClO_4)_2 + 0.5$ M $MgCl_2 > 2$ M $Mg(ClO_4)_2 + 0.5$ M $MgBr_2$, despite the fact that $MgBr_2$ is found to have the maximum conductivity. This observation may be attributed to higher corrosion rates with $MgBr_2$ and $MgCl_2$ [19]. Data could not, however, be obtained in the case of $MgBr_2$ below 0 °C at low concentrations because of freezing of the electrolyte solution.

Conclusions

It is concluded that 2 to 2.5 M $Mg(ClO_4)_2$ aqueous solution is a promising electrolyte for magnesium-based battery systems required to operate over a wide temperature range, and especially at low temperatures.

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