

TECHNICAL NOTE

Reference electrodes and barrier junctions in chloride melts containing magnesium chloride

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1. Introduction

Chloride melts containing magnesium chloride have been used in the electrometallurgy of magnesium metal [1, 2] on an industrial scale since the end of the 19th century. Interestingly, their use as solvents for production of aluminium [3] and extracting manganese [4] and cobalt [4] from the ores found in the ocean floor have only recently been realized.

A knowledge of the chemical and thermodynamic properties of these melts and of the electrode reactions occurring at the representative electrodes requires the measurement of the half-cell potentials of interest. Such a measurement needs a stable, reproducible and easy-to-construct reference electrode. A brief account on the behaviour of a Mg–Mg²⁺ reference electrode of the first kind and of the various barrier junction materials such as graphite fibres, yttria and spinel, which isolate the reference compartment from the main cell in a chloride melt containing magnesium chloride is presented.

2. Mg–Mg²⁺ reference electrode

Electrodes such as Cl[–]–Cl₂ (graphite) and Mg–Mg²⁺ may be employed without introducing any foreign ion impurities into the melt. Although the former electrode has been used [5] in laboratory experiments, the problems encountered in the handling of chlorine gas and maintaining a constant gas pressure over several days prevent an extended use of this reference electrode. For the latter electrode, i.e. the Mg–Mg²⁺ system, only one reference [6] occurs in the literature and no details of fabrication or performance are given. Consequently, a preliminary study was undertaken to evaluate the behaviour of the Mg–Mg²⁺ reference electrode

in a chloride melt containing magnesium chloride.

The cell description and bath composition were presented in an earlier publication [7]. Electrolytically produced molten magnesium (>99.95% pure) was drawn into a rod of diameter 1.5 cm and cut into samples 5 cm long. An 'Ultracarbon' graphite rod, 0.6 cm in diameter and 30 cm long, was screwed into the magnesium sample. This electrode assembly was placed in a quartz tube or a Coors alumina tube, 2.5 cm in diameter (as represented in Fig. 1) such that the molten metal–melt interface was established 2–3 cm from the bottom open end of the outer tube, but still within this tube. The free end of the graphite electrode, which extends about 2–3 cm from the top epoxy-sealed end, was used for an electrical contact. An equilibration vent in the outer tube was situated 10 cm above the melt level but inside the quartz cell which contained the melt.

After placing the Mg–Mg²⁺ reference electrode in 2 M magnesium chloride in a sodium chloride-rich chloride bath at 710 ± 10° C, the electrode potential was monitored against Cl[–]–Cl₂ (graphite) over a period of time. The electrode reached equilibrium within an hour, yielding steady potential readings. However, potential fluctuations were normally observed whenever the cell was disturbed; for example, during breaking the cell top crust, taking bath samples for analysis, adding make-up salt to maintain the bath composition and introducing extra electrodes. Once disturbed, it took 30–60 min for the electrode to reach the same steady-state potential value.

Typical equilibrium potentials for the Mg–Mg²⁺ electrode in ceramic and quartz sleeves are presented in Table 1. Evidently the electrodes in both the ceramic sleeve and quartz

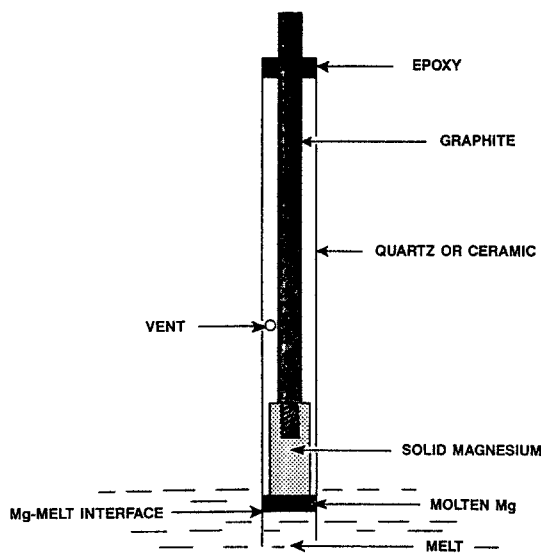
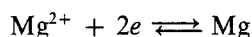


Fig. 1. Mg–Mg²⁺ electrode assembly.

sleeve gave comparable potentials during the first 10 days of operation. However, the latter electrode then began deteriorating and finally ceased to operate after 30 days in service. Such a failure is not surprising because it is well known that quartz reacts with molten magnesium. Interestingly, the performance of Mg–Mg²⁺ in a ceramic sleeve over 30 days on line is rather remarkable.

It is apparent from Table 1 that the equilibrium potential (E) for the reaction



in 2 M magnesium chloride in the chloride melt at 710°C is -2.70 ± 0.02 V. Then, the formal

Table 1. The equilibrium potential of Mg–Mg²⁺ electrode in 2 M magnesium chloride in a sodium chloride-rich NaCl–MgCl₂ bath at 710 ± 10°C

Number of days	In ceramic sleeve (V)	In quartz sleeve (V)
1	-2.71	-2.71
2	-2.70	-2.69
3	-2.71	-2.68
6	-2.71	-2.70
10	-2.72	-2.70
16	-2.70	-2.66
28	-2.69	-2.00
30	-2.69	-

electrode potential (E^0) for the Mg–Mg²⁺ system can be calculated using a Nernst relationship:

$$E^0 = E - \frac{2.303 RT}{nF} \log C_{\text{Mg}^{2+}}$$

where R , T , n , F and C are gas constant, temperature in K, number of electrons ($=2$), Faraday constant and concentration of Mg²⁺ ($=2$ M), respectively. The calculated value for E^0 is -2.73 ± 0.02 V, a good agreement with the literature value [8].

3. Barrier junctions

The work described in the preceding section clearly indicates that a stable electrode potential for the Mg–Mg²⁺ system can be maintained over 30 days. However, once the system is disturbed, it takes a long time to re-establish the original steady state value. Furthermore, it is necessary to minimize the change in Mg²⁺ ion concentration or impurity accumulation in the vicinity of the magnesium–electrolyte interface in the reference electrode compartment during electrolysis with or without cell feeding. To overcome these problems it is necessary to separate the main and the reference compartment with a barrier junction which must be electrically conductive with a low junction potential. Since materials such as lanthanum fluoride [9], thin glass membranes [5] and yttria [10] have been successfully used in molten salt baths, graphite fibres, yttria, quartz and spinel frit junctions were also tested for their stability in this chloride melt containing magnesium chloride. The junction potentials with these materials were also monitored. Although the thin quartz membrane junction was found to be satisfactory for fundamental studies [11], it was not tested in the laboratory-size cell because of the handling problem due to easy rupture of thin membranes. Because Ag–Ag⁺ and Ni–Ni²⁺ reference electrodes provide well-defined, reproducible and reversible half-cell potentials, and have been proposed and used by molten salt chemists, these two systems were used to study the performance of these barrier junctions.

The graphite fibres, Thornel Type P, Panex SWB-8 and Celion, were used as received. A

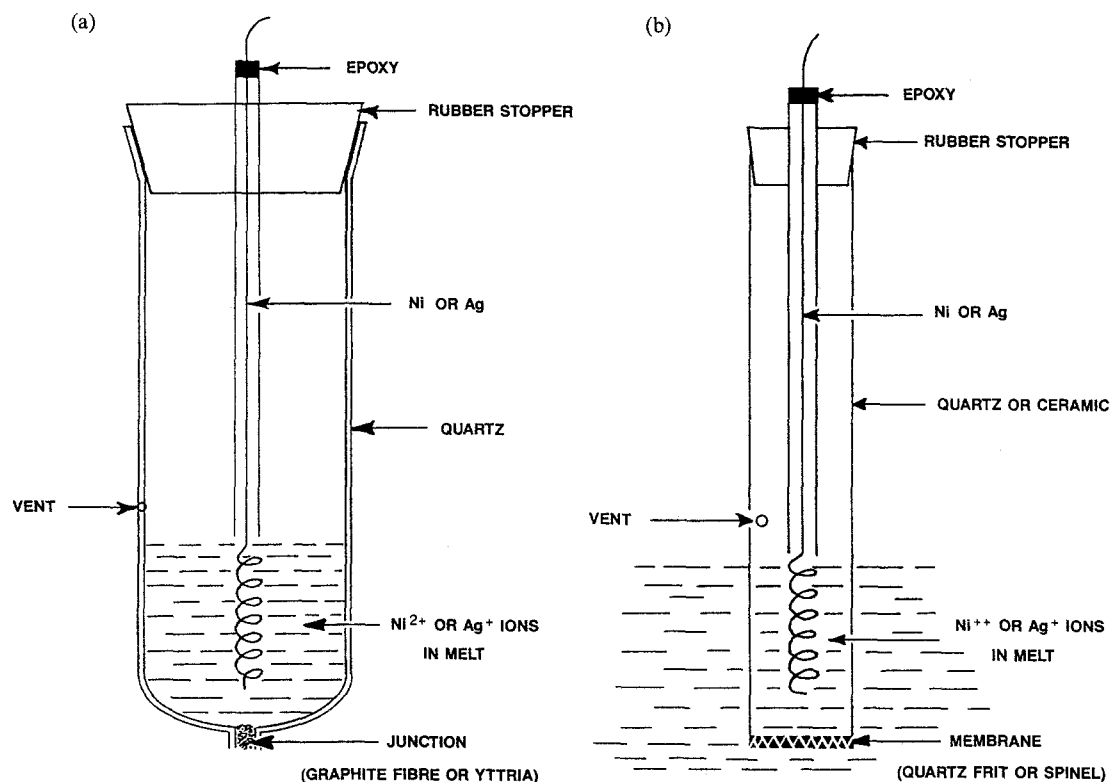


Fig. 2. (a) A typical barrier junction electrode assembly of the fibre type. (b) A typical barrier junction electrode assembly of the membrane type.

bundle of fibres were fused at one end of the quartz tube (2.5 cm in diameter) as shown in Fig. 2a to achieve a junction thickness of about 1 mm. The end of the junction, which is in contact with the cell bath in the main compartment, was cut to make a flat surface. A yttria junction was prepared in a similar way. Spinel mortar T-XYS 40030.00 [12, 13] paste, a phosphate-bonded magnesium aluminum silicate, was applied to one end of a Coors alumina tube (2.5 cm in diameter), dried at room temperature overnight and baked at 200°C for 24 h. The spinel applied end of the Coors tube was cut to obtain a tube with a spinel disc (1–3 mm thick) at the bottom (Fig. 2b). For comparison, a quartz compartment (2–5 cm in diameter) with a quartz frit of #2 porosity was also used. A nickel or silver wire, depending on the electrode system of choice, was placed in all compartments so prepared; typical examples are presented in Fig. 2. A vent hole was provided for the equi-

libration of the melt in the reference compartment with the melt in the main cell.

All barrier junctions appeared intact and undamaged during the 20-day test. The measured average junction potentials are presented in Table 2. It is evident that the yttria barrier junction is most favourable among the materials tested because it prevents the lowest

Table 2. Junction potentials for various barrier junction materials in 2 M magnesium chloride in a sodium chloride-rich NaCl–MgCl₂ bath at 710 ± 10° C

Material	Junction potential (mV)
Panex	160
Celion	169
Thornel	100
Yttria	70
Quartz Frit	140
Spinel Mortar	138

junction potential. Interestingly, the spinel disc membrane gave junction potentials identical to those of the quartz frit with #2 porosity. Spinel, being stable and inert towards molten magnesium [13], would be a better barrier junction to use to fabricate the Mg–Mg²⁺ reference electrode. Among the graphite fibres, Thornel gave a relatively lower junction potential compared with Panex and Celion; this may reflect their resistivities and electrochemical activities.

Unfortunately, experimental problems due to corrosion of electrode materials (silver and nickel) in the reference compartment were rather severe. It was found that the corrosion of electrodes can be minimized by providing a blanket of argon gas in the reference compartment. During this test, nickel appeared to be more stable than silver against corrosion.

4. Conclusions

It has been shown in this work that a Mg–Mg²⁺ electrode can be fabricated easily. The electrode system has an extended stability and life if it is placed in a ceramic tube. Among the various barrier junction materials studied to minimize the mixing of undesired ions or impurities between the reference and the main cell compartments, spinel, yttria and Thornel graphite fibre showed great promise. The corrosion problem of the electrode materials in the reference compartment must be solved prior to using these barrier junctions for the fabrication of the Mg–Mg²⁺ reference electrodes and their application in industrial situations.

Acknowledgements

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