

Electrical Conductivity and Transference Number Measurements of FeO - CaO - MgO - SiO₂ Melts

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Accurate knowledge of the electrical properties of molten salts is paramount in the design of industrial electrolytic cells because joule heating of the electrolyte is central to establishing the thermal balance of the reactor. Molten oxides have been named candidate electrolytes for prospective high-temperature electrochemical processes (1). In particular, Sadoway has speculated on the utility of producing a variety of metals by direct electrolytic reduction of their oxides dissolved in a suitable molten oxide solvent (2). In this vein, the electrical conductivities and transference numbers were measured as a function of FeO concentration in the FeO - CaO - MgO - SiO₂ system.

In response to the lack of a fully satisfactory technique for making high-accuracy conductivity measurements in the melts of interest, a new technique was developed in this laboratory: the coaxial cylinders technique (3, 4). Its applicability to oxide melts had been demonstrated with the MgO - CaO - SiO₂ system (5). In parallel, the use of stepped-potential chronoamperometry for making transference number measurements in oxide melts was examined in detail in connection with the TiO₂ - BaO system (6).

The purpose of the present investigation was to study how electrical conductivity and transference number vary with FeO content in FeO - MgO - CaO - SiO₂ melts. FeO concentration was varied over the composition interval $0 < \text{wt\% FeO} < 20$, where the ratio of CaO:MgO:SiO₂ remained fixed at ~1:1:3 by mass.

The cell design, instrumentation, and experimental procedures are described elsewhere (5,6).

The measured values of electrical conductivity were found to exhibit an Arrhenius-type temperature dependence. Predictably, the conductivity rose with the FeO concentration and was found to vary linearly with same. The ionic transference number fell from a value of unity in the FeO-free melt to 0.7 in the melt containing 20 wt% FeO. With an average value of $\sim 100 \text{ kJ mol}^{-1}$ the apparent activation energy for electrical conduction as determined from the temperature dependence of the measured electrical conductivity decreased as the FeO content of the melt increased. We attribute this to two effects: the rising contribution of electronic conduction, and the modifying effect of ferrous ions in breaking the silicate network.

Comparison with the work of previous investigators is difficult. Unfortunately, most of their results are problematic because they employed various techniques that suffer from the fact that the current path is a function of the electrical properties of the melt, or of the cell, i.e., the electrodes or the crucible. Under these circumstances, calibration with a melt of known electrical conductivity is ineffective: there is no such thing as a "cell constant" when the current path is not strictly defined. This explains the high degree of scatter in the data reported in the literature.

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