

A Robust Alumina Membrane Reference Electrode for High Temperature Molten Salts

Abstract

A new reference electrode for high temperature molten salts (except for fluorides) was conveniently fabricated by sealing the Ag|Ag⁺ (AgCl) couple in a commercial alumina tube whose closed end was ground into a membrane (ca. 0.1 mm in thickness) to facilitate ion conduction. Repeated (>15 times) and prolonged continuous (7 days) tests of this reference electrode in molten chloride and carbonate salts confirmed highly satisfactory and robust performance in terms of stability, reproducibility and reusability over a wide range of temperatures (500~900°C) without any noticeable deterioration. It exhibited ionic resistance (<4 kΩ) decreasing with temperature, but changing insignificantly with the composition of all molten salts tested. A linear relation of potential versus logarithm of mole fraction of NaCl was observed in mixed NaCl-CaCl₂ (slope: 0.1603 V/decade). Salt penetration into the membrane was confirmed by scanning electron microscopy, although no through-pores were observed. These findings are discussed in terms of the membrane and liquid junction potentials, and a mechanism of ion conduction through semi-closed pores (fast and ion-non-selective) and grain boundaries (slow and cation-selective) in series.