Speciation of Rhenium in Chloride Melts: Spectroscopic and Electrochemical Study

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Speciation of rhenium in high-temperature alkali chloride-based melts was studied using electronic absorption and IR spectroscopy of molten salts and diffuse reflectance spectroscopy of quenched melts. Rhenium was added to the melts by anodic dissolution of the metal (at anodic current densities of 0.005-0.05 A/cm²), by reacting Re and ReO₂ with Cl₂ and HCl, and by dissolving K₂[ReCl₆]. The melts included 3LiCl-2KCl and NaCl-2CsCl eutectics, an NaCl-KCl equimolar mixture, and pure NaCl, KCl and CsCl between 450 and 850 °C. Rhenium was present in the melts as Re(IV) hexachloro-ions, [ReCl₆]²⁻; no evidence of species containing rhenium in oxidation states below four was obtained. The kinetics of [ReCl₆]²⁻ disproportionation in molten alkali chlorides were investigated, and the IR spectra of [ReO₄]⁻ ions in molten CsCl-CsI and CsI were measured for the first time.

Key words: Rhenium; Rhenium Chlorides; Chloride Melts; Electronic Absorption Spectroscopy.