

Tungsten Chemistry in Alkali Chloride Melts

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Speciation of tungsten in alkali chloride melts (based on NaCl-2CsCl, NaCl-KCl and 3LiCl-2KCl mixtures) was studied between 550 and 750 °C using electronic absorption spectroscopy. Only W(IV) and W(V) chloro and oxychloro species can be stabilized under the conditions studied. Tungsten(IV) chloride ions are very sensitive to oxide/hydroxide impurities present in the melt. Anodic dissolution of W metal at anodic current densities in the range of 0.005 – 0.1 A/cm² produces only [WCl₆]²⁻ ions that can be electrochemically (on a glassy carbon anode) oxidized to [WCl₆]⁻. Small amounts of oxide ions present in the melt result in a gradual conversion of W(IV) chloro species into W(IV) oxychloro species. In the presence of O₂ in the atmosphere [WCl₆]²⁻ is oxidized into the tungsten(V) species [WOCl₅]²⁻. Dissolution of tungsten hexachloride, WCl₆, in an NaCl-2CsCl melt initially yields [WCl₆]²⁻ (due to disproportionation). Reaction of metallic tungsten with Pd(II)-containing melts results in the formation of [WCl₆]²⁻ species. The main spectroscopic parameters of [WCl₆]²⁻ and [WCl₆]⁻ complex ions were calculated.

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