

Influence of Second Coordination Sphere on the Kinetics of Electrode Reactions in Molten Salts

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The influence of the second coordination sphere on the electroreduction of hafnium complexes to hafnium metal, and the redox reaction $\text{Eu(III)} + e^- \rightleftharpoons \text{Eu(II)}$ in alkali halide melts was studied. It is shown that the large caesium cations in the melt reduce the transfer and the diffusion coefficients as well as the heterogeneous rate constants for charge transfer of hafnium complexes. The standard rate constants for the europium redox reaction increase when going from NaCl-KCl to CsCl. The different influence of the second coordination sphere on the electrode reactions is explained by different limitation stages for electron transfer.

Key words: Melts; Second Coordination Sphere; Cyclic Voltammetry; Heterogeneous Rate Constants; Standard Rate Constants.