

ELECTROCHEMICAL BEHAVIOR OF ZIRCONIUM IN LiCl - KCl EUTECTIC MOLTEN SALT

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ABSTRACT

Nuclear fission energy increasingly represents a potentially important option for generating clean, CO₂-free electricity and the nuclear community is considering advanced reactor and fuel cycle technologies. Pyroelectrochemical processes based on molten salt electrochemistry have become important for the potential recycle of metal and other advanced nuclear fuels. Zirconium is one of the troublesome fission products that is expected to be present in such used fuels and hence it is important to acquire an understanding of its electrochemistry in molten salts. The present investigation addresses the electrochemical reduction of Zr⁴⁺ in LiCl - KCl eutectic molten salt using transient techniques such as cyclic voltammetry (CV), constant-current chronopotentiometry (CP) and square wave voltammetry (SWV) at 425, 475 and 525 °C. The CV data clearly indicate reduction of Zr⁴⁺ proceeds through an *initial* adsorption process followed by two or three reaction steps dependent on the temperature. Results show three previously unobserved reaction steps at 425 and 475 °C, possibly due to improved pretreatment of the salt. The first cathodic peak is observed at -1.18 V (vs. Ag/AgCl). The second and third peaks are observed at -1.26 and -1.33 V (vs. Ag/AgCl), respectively with a separation of 60-70 mV. The CV data at 525 °C show only two cathodic peaks at about -1.1 and -1.25 V (vs. Ag/AgCl) which may indicate the effect of temperature on the mechanism of the electrochemical process. The overall reaction mechanism assessed by these electrochemical techniques will be presented. Moreover, electrodeposition of zirconium on aluminium metal will also be presented along with XRD analysis of the salt residue and zirconium-aluminium alloy. Finally, the kinetics of the electrochemical process have been studied using Electrochemical Impedance Spectroscopy and the results analyzed using the Randles-Ershler equivalent circuit model to determine the charge-transfer resistance (*R_{ct}*).