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Title of paper Cyclic Voltammetric Study of the Reduction of U(III) to Uranium Metal in Molten $LiCl-NaCl-CaCl_2-BaCl_2$

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The electrochemical reduction of U(III) to uranium metal in molten $LiCl-NaCl-CaCl_2-BaCl_2-UCl_3$ electrolyte was investigated, using cyclic voltammetry. The reaction was reversible and controlled by diffusion mass transfer, both at low-carbon steel and molybdenum electrodes. The rate increased with UCl_3 concentration up to about 3.4 mol %, and with temperature over the range 436-528°C. Standard potentials ranged from -1.07 to -1.50 V vs. Ag/AgCl; the U(III) diffusion coefficients from 0.5 to 4.0×10^{-6} cm^2/s.

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CYCLIC VOLTAMMETRIC STUDY OF THE REDUCTION OF U(III) TO URANIUM METAL IN MOLTEN $LiCl-NaCl-CaCl_2-BaCl_2-UCl_3$

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Introduction

Cyclic votlammetry was used to investigate the electrochemistry of the reduction of UCl_3 to uranium metal in molten $LiCl-NaCl-CaCl_2-BaCl_2$ (49.7-8.0-26.5-15.8 mol %) containing dissolved UCl_3. The purpose of the study was to obtain information on the kinetics of the reaction, which will be used in the design of electrorefining equipment for the reprocessing of core and blanket fuel discharged from the Integral Fast Reactor (IFR). The electrorefining operation employs the above salt as the electrolyte and a liquid cadmium pool as the anode.

Literature values for the standard potentials of the U(III)/U(0) couple in LCl-Kcl, NaCl-KCl, and $NaCl-KCl-MgCl_2$ eutectic salts have been critically reviewed by Plambeck (1). Comprehensive reviews of the electrochemistry of uranium have been published by Martinot and Caligara (2,3). Polarographic studies of uranium species in molten LiCl-KCl and $LiCl-KCl-MgCl_2$ eutectics have been reported by Hill et al. (4).

Experimental

The electrochemical cell comprised (a) a low-carbon steel crucible (vol., 325 cm^3), which served as the cell container, (b) a working electrode consisting of a 0.32-cm-diameter metal (either molybdenum or low-carbon steel) rod encased in an alumina tube in such a way that an apparent surface area of 0.079 cm^2 was exposed to the electrolyte, (c) a liquid cadmium counter electrode, and (d) a Ag/AgCl reference electrode. The cell was located in a furnace well in the floor of a high-purity, helium-atmosphere glove box. The cell temperature was measured with a calibrated Chromel-Alumel thermocouple.

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The UCl_3 in the electrolytic was generated in situ by dissolving metallic uranium in the liquid cadmium, and then adding $CdCl_2$ to the salt phase.

Single-sweep and cyclic voltammetric scans were made with a potentiostat (PAR Model 173) coupled to a PAR Model 175 universal programmer. Current-voltage curves were recorded with a Hewlett-Packard Model 7044-A recorder.

Results and Discussion

Figure 1 shows typical cyclic voltammograms for the reduction of U(III) to the metal at a molybdenum electrode at 465°C. A simple, well-defined cathodic current peak (i_{pc}) was observed. The anodic current peak, which is sharp and symmetrical, is characteristic of the oxidation of a solid deposit from an electrode surface.

The cathodic peak current (i_{pc}) was linearly proportional to the square root of the potential scan rate ($v^{1/2}$). Plots of i_{pc} vs. $v^{1/2}$ for various temperatures (436 to 528°C) and for the two different cathode materials (molybdenum and steel) were linear and passed through the origin. In addition, the peak current potentials and the separations between the peak and half-peak potentials (15 to 20 mV) were independent of potential scan rate. These results indicate that the charge-transfer reaction of the U(III)/U(0) couple is reversible and occurs under diffusion-controlled conditions.

In general, the reduction rate of U(III) increased with increasing temperature. Over a temperature range of 436 to 520°C, the increase in the magnitude of the reduction peak current of U(III) with temperature can be approximated by a linear relationship. The temperature coefficients for U(III) under these conditions were 1.1×10^{-2} mA/°C at the steel electrode and 6.1×10^{-3} mA/°C at the molybdenum electrode.

When the UCl_3 concentration in the salt was increased from 1.8 to 3.4 mol %, the reduction peak current increased by a factor of four to five. Further increases to 5.3 and then to 6.7 mol %, however, caused no significant change from the rate at 3.4 mol %.

Figure 2 shows that the separation between the cathodic and anodic current peak potentials increased consistently, and all the peak potentials shifted in a positive direction with increasing UCl_3 concentration. The reduction peak potential for U(III) shifted from -1.5 V (vs. Ag/AgCl) at 1.8 mol % UCl_3 to about -1.2 V at 6.7 mol %.

Standard potentials obtained for the U(III)/U(0) couple in this electrolyte ranged from about -1.07 to -1.50 V, depending on the experimental conditions.

Values of the diffusion coefficient for U(III) ions in this electrolyte at 465°C were estimated at 0.5×10^{-6} to 4.0×10^{-6} cm^2/s, depending on the UCl_3 concentration.

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In general, the results of this study are in reasonable agreement with earlier data obtained with other molten chloride electrolytes (1-4).

Acknowledgment

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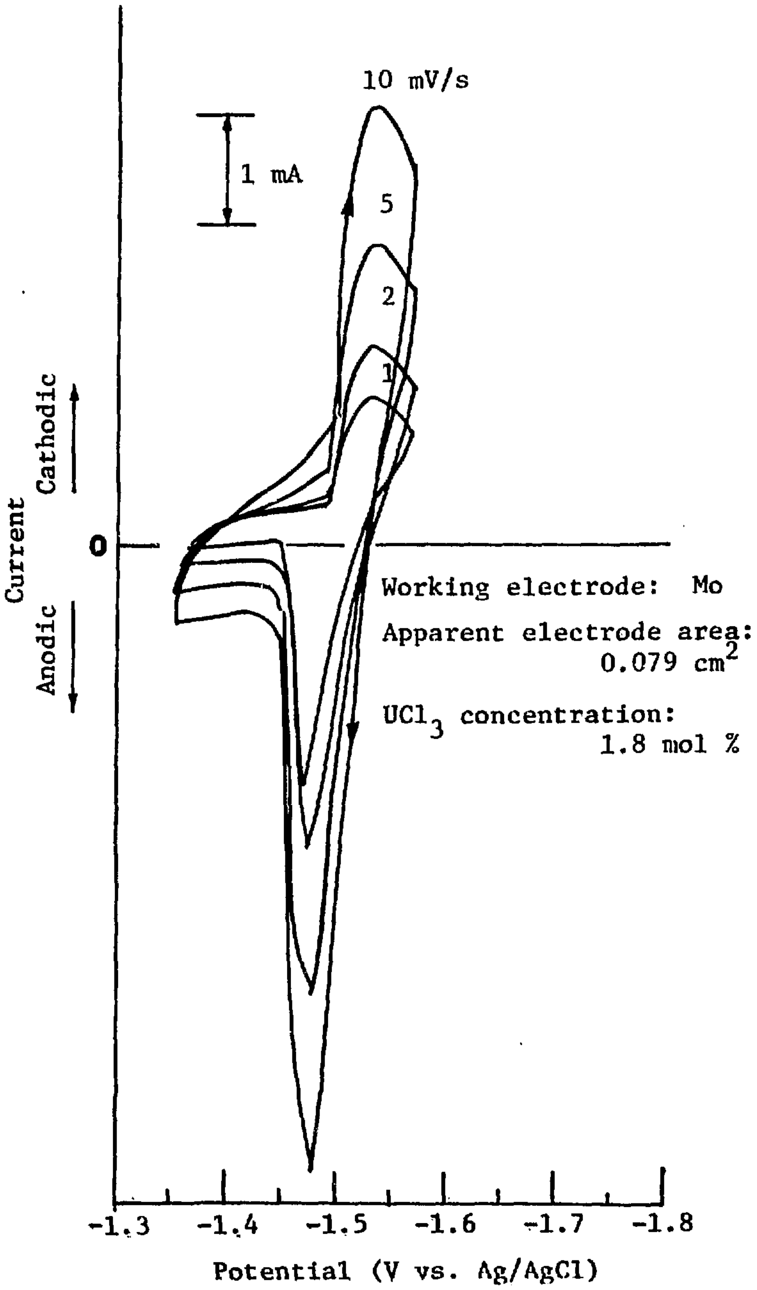

Fig. 1. Effect of Potential Scan Rate on Cyclic Voltammograms for the Reduction of U(III) at 465°C.

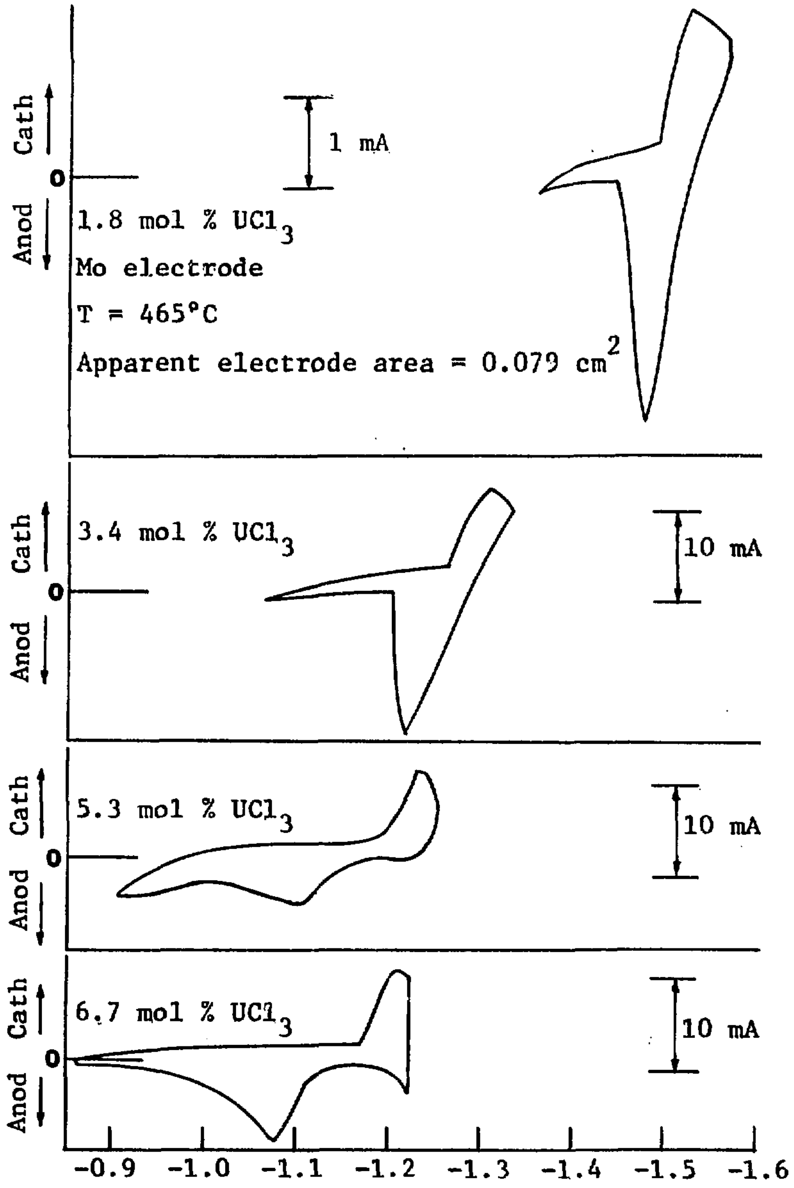

Fig. 2. Effect of UCl_3 Concentration on Voltammograms for the Reduction of U(III) at 2 mV/s Scan Rate.