Cathodic Behavior of Ce(Ⅲ) ion in NaCl-2CsCl Melt

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An electroanalytical study was carried out for cerium ion Ce(III) reduction in NaCl-CsCl melt, by cyclic voltammetry (CV) and square wave voltammetry (SWV). A tungsten disk electrode was used as the working electrode, and Ag/AgCl electrode was used as the reference electrode. All the experiments were carried out under the atmosphere of Ar, and at the temperature of 873K.

Figure 1 shows a typical cyclic voltammogram for the reduction of a solution of cerium tricholiride. Two cathodic peaks, (A) and (B), were observed at the cathodic sweep, and followed by two anodic peaks, (A') and (B') at the reverse sweep. A typical square wave voltammogram is shown in figure 2. It is clear that the current-potential curve is bell-shaped and symmetrical about the half-wave potential. There are two waves during potential sweep. Both the results of cyclic voltammetry and square wave voltammetry indicate that the electroreduction of Ce(Ⅲ) ion in the solvent proceeds via a two step process. The results of the calculation on the electron number for the electrode steps of (A) / (A') and (B)/(B') were around 1 and 2, respectively. It can thus be conclude that (A) / (A') corresponds to a soluble-soluble system Ce(Ⅲ)/Ce(Ⅱ), and (B) / (B') are associated to the formation of metallic Ce and its reoxidation:

$$Ce^{3+} + e = Ce^{2+}$$
$$Ce^{2+} + 2e = Ce$$

This two-step processing mechanism is different from the reported mechanism of Ce(III) reduction in molten chloride of LiCl-KCl, $CaCl_2$-KCl [1,2]. According to these authors, the electrochemical reduction of Ce(Ⅲ) ion is one step process. The different electroreduction mechanism probably results from the difference of solvent molten salts system.

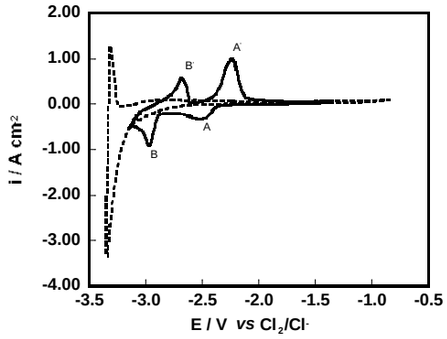

Figure 1 Typical cyclic voltammogram for the reduction of cerium trichloride on a tungsten electrode (7.8×10^{-5} cm^2) in the NaCl-2CsCl mixture at 873 K. Sweep rate 0.6 V s^{-1}.

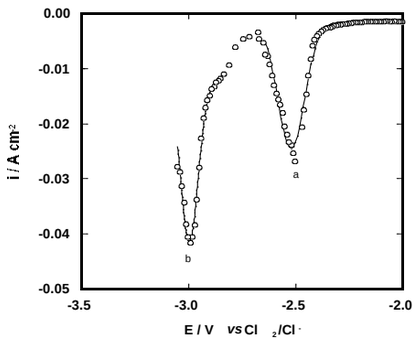

Figure 2 A typical square wave voltammogram recorded on a tungsten electrode (7.8×10^{-5} cm^2) at 873 K. Square wave amplitude 20 mV, frequency 50 Hz.

References

1. Y. Castrillejo, M.R. Bermejo, R. Pardo and A.M. Martínez, *J. Electroanal. Chem.* **522** (2002) 124
2. C. Caravaca, P. Díaz Arocas, J.A. Serrono and C. González, 6th Exchange Meeting, Mould, Spain, 2000, 625