

Electrochemistry of Ta(V) in Lewis Basic TaCl₅-EMIC Low Temperature Molten Salts

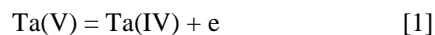
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Molten salt systems provide a potential of the application for electrodeposition of metals and alloys, which are difficult to deposit from conventional aqueous media. In fact, some kinds of metals (Al, Mo, W, Ta) and alloys (Al alloys), of which the electrodeposition is impossible from aqueous solutions, can be electroplated from inorganic chloride and fluoride melts. However, its handling at high temperature made it difficult to use the molten salt system as a conventional electroplating method. The disadvantage can be dissolved by using the molten salt consisting of an anhydrous metal chloride and an organic salt such as EMIC (1-methyl-3-ethyl imidazolium chloride) or BPC (n-butylpyridinium chloride), because such a mixture shows a low melting point compared to the relevant inorganic melts. One of the typical examples is a Lewis acidic AlCl₃-EMIC melt, in which the electrodeposition of Al and Al alloys is possible at room temperature. Besides the chloroaluminate melt, a family of ambient and low temperature ionic liquids formulated from EMIC and anhydrous metal chloride have been reported: AgCl, CuCl, LiCl, CdCl₂, CuCl₂, SnCl₂, ZnCl₂, LaCl₃, YCl₃, SnCl₄, and TiCl₄.¹ We also screened other metal chlorides which could form room temperature molten salts by mixing with EMIC, and it was found that the mixture of anhydrous tantalum(V) chloride with EMIC produced a novel ionic liquid at near room temperature at some compositions.² In this paper, the cathodic reactions of Ta(V) in a Lewis basic TaCl₅-EMIC melt were investigated by using various voltammetric techniques to access the possibility of the melt for use as an electrolyte for tantalum plating.

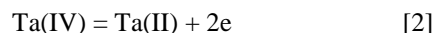
Anhydrous TaCl₅ of 99.9 % purity was used as received. The EMIC was purified according to the method described in the previous paper.³ The known amounts of TaCl₅ and the purified EMIC were loaded into a glass tube, then the glass tube was sealed under vacuum and was settled in a furnace at 373 K for a few hours to obtain 33.3:66.7 mol% TaCl₅-EMIC melts. The electrochemical reduction of Ta(V) in the TaCl₅-EMIC melt was investigated using a Pyrex glass cell. The main compartment of the cell was equipped with a Pyrex glass shrouded platinum or tungsten wire as the working electrode (0.196 mm²) and coiled tungsten wires as the counter and quasi-reference electrodes. The reference electrode was an aluminum wire of 99.999% purity immersed in an AlCl₃-EMIC (66.7:33.3 mol%) melt, which was isolated from the main compartment by an individual Pyrex glass tube having a thin glass membrane at the bottom. All potentials reported herein are referred to the aluminum electrode. All electrodes were fixed to the cell by glass sealing, and both compartments were completely sealed under vacuum after loading TaCl₅-EMIC or AlCl₃-EMIC melts.

The electrochemical reduction of Ta(V) in a Lewis basic TaCl₅-EMIC (33.3:66.7 mol%) melt was investigated at 373 K. As shown in Fig. 1, two cathodic waves (A, B) and two anodic waves (C, D) were observed in the cyclic voltammogram. The normal pulse voltammogram of the basic melt was also measured, and

two plateaus for waves A and B were observed in the voltammogram. The wave shape analysis of the normal pulse voltammogram was carried out following a usual manner. The plots of potential vs. $\log \{(i_a - i)/i\}$ was linear for each of waves A and B, indicating that the stoichiometric ratio of redox couple is 1:1 for both cases. The number of electrons involved in each reaction was calculated from the slope of the straight line. The results suggested that the reaction for wave A was one-electron transfer step, while that for wave B contained two-electron transfer. From these results, we reasonably proposed that the first reduction of Ta(V) in the basic melt was



and the second was



Although the reactions for waves A and B in the basic melt had some irreversibility. A further reduction of Ta(II) was not confirmed in the basic melt on the time scale of voltammetric measurements, and constant current electrolyses of the basic melt gave no electrodeposit on the cathode.

We further accessed the probability of tantalum electrodeposition by adding LiF into the melt. The LiF addition resulted in the appearance of two new cathodic waves at potentials negative than that of wave B. These cathodic waves suggested that further reductions of Ta(II) were possible to proceed by the addition of LiF. The galvanostatic electrolyses of the LiF-added melt to obtain some electrodeposits were then performed. The results

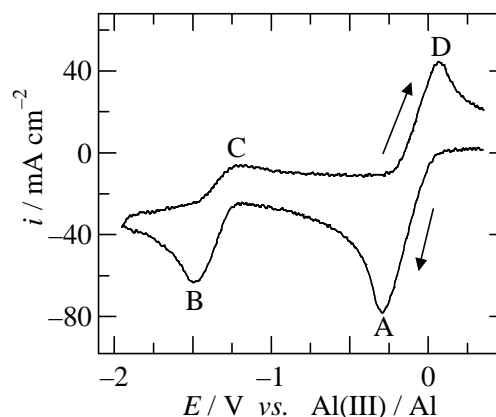


Fig. 1 A cyclic voltammogram of a TaCl₅-EMIC (33.3:66.7 mol%) melt obtained with a platinum electrode at 373 K. Scan rate 0.1 V s⁻¹

will be also shown in this paper.

References

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- 2 M. Matsunaga, M. Morimitsu, and T. Matsuo, *Proceedings of the 7th China-Japan Bilateral Conference on Molten Salt Chemistry and Technology*, p. 209 (1998).
- 3 M. Matsunaga, T. Kitazaki, K. Hosokawa, S. Hirano and M. Yoshida, in *Proceedings of the Ninth International Symposium on Molten Salts*, The Electrochemical Society, NJ, PV 94-13, p. 422 (1990).