

INVESTIGATION OF KINETICS OF ELECTRODE PROCESSES IN HALIDE MELTS, CONTAINING BERYLLIUM, VANADIUM, NIOBIUM AND HAFNIUM

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Investigation of the processes at the interface "electrode-melt" and determination of their mechanisms are necessary for understanding of the structure of this unique class of ionic liquids and comparison with the theoretical predictions concerning the nature of the heterophase electrochemical reactions. Apart from the pure scientific value the information about the kinetics of electrode reactions can also be used for solving problems arising in organising electrolytic production and refining the metals which cannot be obtained by the "classical" aqueous electrochemical techniques. In the present study the electrochemical reactions involving beryllium, vanadium, niobium and hafnium were studied.

In our work we combined galvanostatic commutational method with different types of chronopotentiometry, *i.e.*, classic, reversible and that with programmable current change. A galvanostat was constructed, which allows obtaining highly stabilised current with the maximum amplitude up to 30 A and the continuous impulse front up to 1 μ s. A custom-built automated computer-controlled set-up, based on an Intel™ Pentium™ processor and equipped with the digital-to-analogue and analogue-to-digital converters, allowed greater flexibility in selecting various types of voltamperometric experiments and methods of registering the potential of working electrode. This computerised set-up permitted obtaining new information about the kinetics of the electrode processes in halide melts.

A special procedure for recording the anodic and cathodic polarisation curves under a variety of experimental conditions has been developed. We used a vibrating electrode in order to insure the most effective return of the electrolyte in the near electrode layer to the initial state after each cycle.

Several methods were used for preparing chloride melts containing the ions of the studied metals, *i.e.*, anodic dissolution of the metals, direct chlorination of the metals in the melts with chlorine or hydrogen chloride, or "dry" chlorination with chlorine or carbon tetrachloride. The experiments were performed in the melts based on the LiCl-KCl eutectic, NaCl-KCl equimolar mixture, individual NaCl and KCl. Additionally the behaviour of beryllium was studied in chloride-fluoride melts, where beryllium was added into chloride melt as BeF₂. Working electrodes were made of studied metals, glassy carbon or molybdenum encapsulated into beryllium oxide. All the measurements were performed against chlorine reference electrode. The experiments were conducted between 400 and 900 °C and the concentration of studied metals in the melts up to 10 wt. %.

It was found that under the studied conditions the processes of anodic dissolution and cathodic deposition occurred in the diffusion regime. An average number of electrons taking part in the reactions was determined. In case of beryllium the formation of chloride and chloride-fluoride complexes had strong influence on the discharge and ionisation of ions of this metal. The equations

describing the chronopotentiograms recorded during applying and switching off the polarisation current and taking into account the formation of complexes were derived.

The possibility of co-existence of complexes containing metal in different oxidation states was confirmed when analysing the red-ox processes in vanadium-, niobium- and hafnium-containing melts, and the conditions favourable for the formation of ions of a particular oxidation state were determined. It was also found that molybdenum substrate was not indifferent towards the melts containing vanadium(III) and niobium(V).

It was found that at high current densities the anodic dissolution was complicated by various types of salt passivation. The effect of the nature of metal, its concentration in the melt, temperature and the presence of the ions containing the metal in the higher oxidation states on the type of the salt passivation was analysed.

The phenomenon of increased growth of the surface of cathodic deposit at high current densities was established. The influence of the alkali metals formed at the cathode on the character of the polarisation curves (formation of the so-called "second wave") and the chronopotentiogram recorded upon applying current was studied. Typical examples of the potentiograms obtained in the beryllium-containing melts and showing the "second wave" are shown in Fig. 1. In the process of studying cathodic polarisation in vanadium-containing melts it is also important to distinguish between the "limiting diffusion current density" and the "current density corresponding to the beginning of the increased growth of the cathodic deposit".

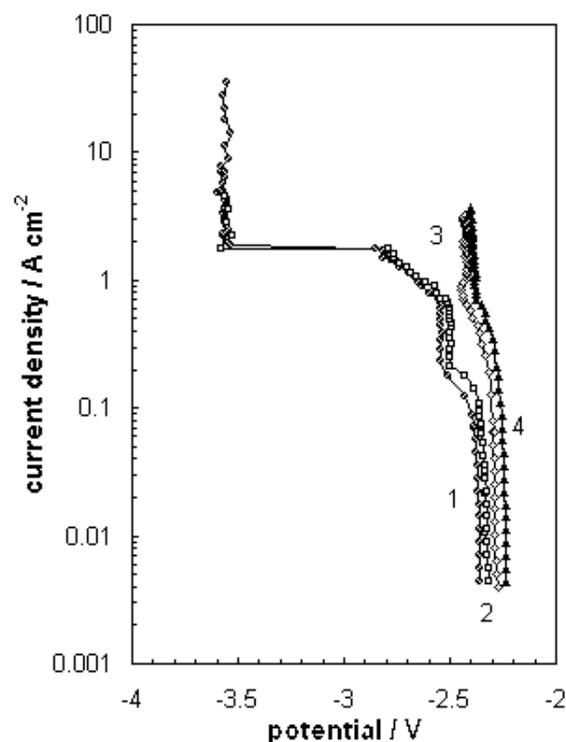


Fig. 1. Cathodic polarisation curves of beryllium in LiCl-KCl-BeCl₂ melt at 400 °C. Concentration of BeCl₂ in the melt, wt.%: 1, 3.0; 2, 4.2; 3, 8.0 and 4, 11.0.