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Electrochemical studies of zirconium and hafnium in alkali chloride and alkali fluoride–chloride molten salts

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The electrochemical reduction of zirconium and hafnium in alkali chloride or fluoride–chloride molten salts on platinum electrodes has been investigated by means of linear and cyclic voltammetry. It has been found that fluoride ions greatly influenced the reduction of zirconium and hafnium in fluoride–chloride melts. It has been proposed that the mechanism for reduction of zirconium and hafnium in baths containing a low concentration of fluoride compounds is different from the mechanism in baths containing a higher fluoride concentration.

1. Introduction

The molten salt electrochemistry of zirconium and hafnium, including the cathodic and anodic process mechanism, the electrodeposition from alkali chloride, fluoride or chloride–fluoride mixed fused melts, has been investigated by several researchers [1–8]. The electrochemical behaviour of zirconium and hafnium in fused salts is complicated by the lower valent oxidation states of zirconium and hafnium and by the effects of the anions and cations on zirconium and hafnium complex stability [4–8].

Polyakova and Stangrit [9] and Smirnov *et al.* [10] proposed that the cathodic reduction of zirconium in chloride melts comprises two-electroreduction reactions $Zr^{4+} + 2e^- \rightarrow Zr^{2+}$ with the formation of soluble zirconium dichlorides and deposition of metallic zirconium ($Zr^{2+} + 2e^- \rightarrow Zr$) on the cathode. In the literature [11], a two-step mechanism of zirconium reduction in chloride molten mixture is also determined at 973 K ($Zr^{4+} \rightarrow Zr^{2+} \rightarrow Zr$), the first step being an irreversible reaction.

In their own study of the electrochemical reduction of $ZrCl_4$ in molten NaCl, CsCl, KCl–NaCl [7], Basile *et al.* claimed that the reduction was dependent on the nature of the anions and cations in the molten bath. They considered the reduction of $ZrCl_4$ in KCl–LiCl at 973 K to be Zr^{4+} (complex) $\rightarrow Zr^{2+} \rightarrow Zr$, while they observed that there were four waves for the reduction of $ZrCl_4$ in NaCl at 1093 K: the first wave was due to Zr^{4+} (complex) $\rightarrow Zr^{2+}$; the second, Zr^{4+} (gas state) $\rightarrow$ Zr; the third, Zr^{4+} (complex) $\rightarrow$ Zr; and the fourth, $Zr^{2+} \rightarrow Zr$.

According to the data obtained by Smirnov *et al.* [10], the mechanism of the cathodic process in chloride–fluoride melts is

$$Zr^{4+} + e^- \longrightarrow Zr^{3+}; \qquad (1)$$

$$Zr^{3+} + 3e^- \longrightarrow Zr. \qquad (2)$$

Winand [12] discovered a one-step Zr^{4+} reduction to metallic zirconium in NaCl or $CaCl_2$–$BaCl_2$ melts with ZrF_4. Polyakova and Stangrit [9] also suggested a similar reduction mechanism for zirconium reduction in KCl–NaCl–K_2ZrF_6 molten mixtures.

Solutions of K_2ZrF_6 in equimolar KCl–NaCl at 973 K to 1073 K under argon atmosphere show three different decomposition potentials assigned to the reduction of Zr^{4+} to a lower oxidation state, of Zr^{4+} to zirconium metal, and of $K^+ \rightarrow$ K metal [13]. The polarization curves for such a solution [14] find explanation in terms of the reduction process, $Zr^{4+} \rightarrow Zr^{2+} \rightarrow Zr$.

Little has appeared on analogous hafnium systems, but there is one report [15] on the electrochemical study of hafnium in equimolar KCl–NaCl with $HfCl_4$ at 973 K to 1173 K. It was proposed by the authors that the cathodic reduction process in the temperature range from 973 K to 1123 K at the concentration below 10^{-3} mole fraction is

$$Hf^{4+} + e^- \longrightarrow Hf^{3+} \text{ (soluble)}, \qquad (3)$$

$$Hf^{3+} + e^- \longrightarrow Hf^{2+} \text{ (soluble)}, \qquad (4)$$

$$Hf^{2+} + 2e^- \longrightarrow Hf \text{ (insoluble)}. \qquad (5)$$

However, in the temperature range from 1123 K to 1173 K, the reaction $Hf^{4+} \rightarrow Hf^{2+} \rightarrow Hf$ was the principal one.

In our previous work [16–19], we have investigated the electrochemical cathodic reduction and the anodic dissolution of titanium in chloride and fluoride–chloride melts and the interaction between titanium and the molten mixture. It was found that fluoride ions in the molten bath had a considerable effect on these reactions.

In this work, we describe electrochemical studies of zirconium and hafnium in chloride or fluoride–chloride molten salts. We also investigate a new method of separating hafnium and zirconium by

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direct electrolysis based on the preferential formation of a hafnium fluoride complex in chloride–fluoride melts. It was found that hafnium and zirconium can be partially separated using controlled potential electrolysis by adjusting the fluoride concentration in the bath. The separating method and our results will be presented in a further paper [20].

2. Experimental procedure

We have already described the experimental cell used in this work [16]. All the experiments were conducted in a protective purified argon atmosphere. The auxiliary electrode was pyrolytic graphite (3mm in diameter) with a much larger surface area than that of the working electrode. The working electrode was a platinum electrode which was prepared from platinum wire of 0.5 mm diameter. This was washed with alcohol, acetone, distilled water, dried and then sheathed in alumina tube with alumina cement. The surface area of the working electrode was 0.08 cm^2. The reference electrode was a silver wire immersed in a solution of 0.1 M AgCl in equimolar KCl–NaCl melts which was placed in a very thin mullite tube (4 mm in diameter). It was observed that this reference electrode was very steady and had a good reproducibility.

An equimolar KCl–NaCl mixture was used as supporting electrolyte. This was prepared from alkali halides of high chemical purity, heated to their melting point in a vacuum to eliminate moisture, then cooled and kept in a dried argon atmosphere. High-purity KF was dried and used to adjust the fluoride concentration in the bath to investigate the effects of fluoride ions on the electrochemical behaviour of zirconium and hafnium.

Chemical purity zirconium tetrachloride ($ZrCl_4$), zirconium or hafnium tetrafluoride (ZrF_4 or HfF_4) and potassium zirconium fluoride were also used in this experiment.

Potentiostatic control was achieved by a conventional potentiostat. Cyclic or linear voltammetry with scanning rates from 0.01 V s^{-1} to 1 V s^{-1} were adopted in this study.

3. Results and discussion

3.1. *Electrochemical studies of zirconium in the molten salts*

Typical cyclic voltammograms of zirconium in equimolar KCl–NaCl with $ZrCl_4$ at temperatures of 973 K and 1033 K on a platinum electrode are demonstrated in Fig. 1. The cyclic behaviour of zirconium at 973 K (Fig. 1a) is very similar to that at 1033 K (Fig. 1b). Comparison of the results given in Fig. 1 with the cyclic voltammogram of a platinum electrode in equimolar KCl–NaCl melts prior to addition of $ZrCl_4$ at the same temperature shows that the current increase at potentials of less than − 1.5 V is associated with the alkali metal (potassium or sodium) deposition.

Two well-defined main peaks were observed on the cathodic side of the cyclic voltammograms. On the anodic side, three main reoxidation peaks appeared. It seemed that no cathodic and anodic peak pairs existed except the anodic stripping peak 5 corresponding to the oxidation reaction of peak 3. Different linear sweep voltammograms of zirconium reduction in the melts at 973 K to 1033 K on a platinum electrode for various values of the scanning rates were also performed. It was observed that the peak potentials of peaks 2 and 3 are approximately independent of the scanning rates and the peak current, I_P, for the first main peak (peak 2) was found to be proportional to the square root of the scanning rate at the platinum electrode. It can be concluded that the electroreduction process of zirconium in the chloride molten salts is reversible. Then, the following equation [21] can be applied for the estimation of the electron numbers involved in these reactions:

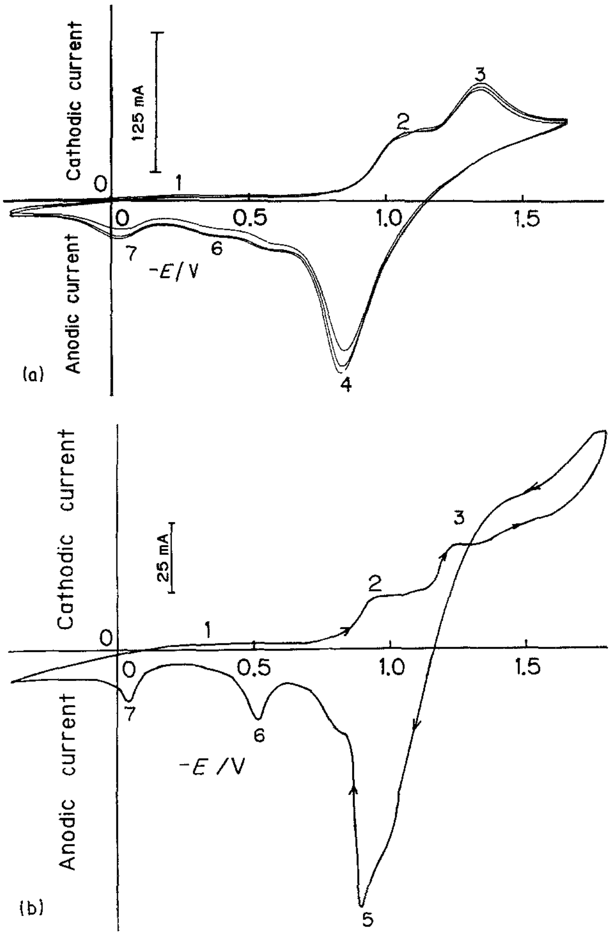

Fig. 1. Cyclic voltammograms of zirconium in KCl–NaCl melts with 4.76 wt % $ZrCl_4$ in a platinum electrode of surface area 0.08 cm^2. (a): 973 K, 0.5 V s^{-1}; (b): 1033 K, 0.05 V s^{-1}.

$$E_{PC/2} - E_{PC} = 2.2RT/(nF)$$

where E_{PC}, $E_{PC/2}$ are the cathodic peak potential and the half-peak potential, respectively. The calculation of the electron numbers according to Equation 1 indicated that the electron number, n_2, related to the first main peak (peak 2) was 2.1 ± 0.25, and n_3, corresponding to the second main peak (peak 3), was 2.2 ± 0.3.

The plot of E against ln $[(i_d - i)i]$, where i_d is the

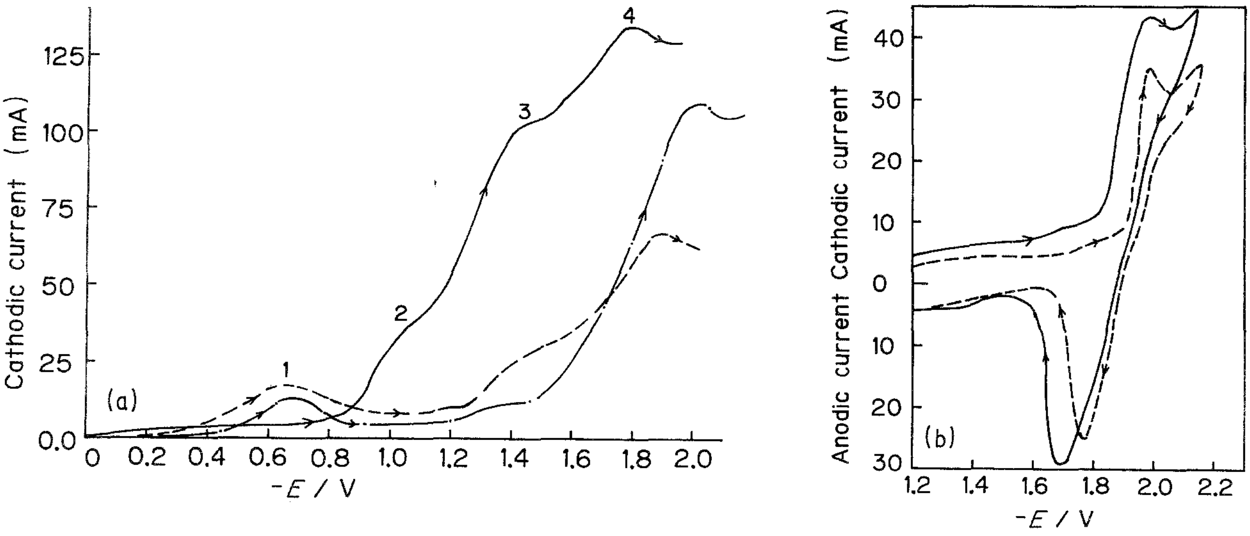

Fig. 2. The effects of fluoride concentration on the linear sweep voltammetry of zirconium in KCl–NaCl melts with 1.86 wt % Zr^{4+} and different composition of KF on a platinum electrode (0.08 cm^2) at 973 K. (a) (——) $X_{F-}/X_{Zr4+} = 1.07$, sweep rate = 0.33 V s^{-1}; (----) $X_{F-}/X_{Zr4+} = 4.0$, sweep rate = 0.33 V s^{-1}; (—·—) $X_{F-}/X_{Zr4+} = 6.0$, sweep rate = 0.20 V s^{-1}. (b) (——) $X_{F-}/X_{Zr4+} = 16$; (– – –) $X_{F-}/X_{Zr4+} = 22$.

limiting current density for peak 2 was a very good linear relation. The electron number, n_3, was also estimated to be 2.08 from the slope [$= RT/(nF)$]. Flengas *et al.* [5–6] pointed out that Zr^{4+} ions in alkali chloride melts exist as the complex, $ZrCl_6^{2-}$. Thus, according to the electron numbers, it is considered that the main cathodic process in KCl–NaCl–$ZrCl_4$ has double two-electron steps.

$$\text{Peak 2, } Zr^{4+} \text{ (chloride complex)} + 2e^- \longrightarrow Zr^{2+}, \tag{6}$$

$$\text{peak 3, } Zr^{2+} + 2e^- \longrightarrow Zr \tag{7}$$

That is in agreement with the data [7, 9–10]. The small peak pair (peaks 1 and 7) as shown in Fig. 1 was considered to be due to the existence of other zirconium chloride complexes besides the main complex, $ZrCl_6^{2-}$ [2, 7].

Typical linear sweep voltammograms of the cathodic reduction of Zr^{4+} (complex) in KCl–NaCl–$ZrCl_4$ melts with different concentrations of KF are shown in Fig. 2. It can be concluded that the reactions at peaks 2 and 3 shown in Fig. 2 are the reactions: Zr^{4-} (chloride complex) + $2e^- \rightarrow Zr^{2+}$, and Zr^{2+} (chloride complex) + $2e^- \rightarrow Zr$, respectively from comparison of the cycle in Fig. 2 with the results depicted in Fig. 1. Also, a new peak (peak 4) appeared when small amounts of KF($X_{F-}/X_{Zr4+} = 1.07$) were added into equimolar KCl–NaCl melts with $ZrCl_4$.

According to the data in Fig. 2, the currents at peaks 2 and 3 decreased as the ratio (X_{F-}/X_{Zr4+}) of F^- mole fraction to Zr^{4+} mole fraction in the melts increased. When the ratio was equal to 6, the currents associated with the reduction of zirconium chloride complex ions ($ZrCl_6^{2-}$) could not be detected. This implied that there exists only small amounts of $ZrCl_6^{2-}$ in chloride–fluoride molten salts in which $X_{F-}/X_{Zr4+} = 6$. On the other hand, the currents at peak 4 increased with the increase of fluoride concentration. As the ratio became larger than 3, a small new peak (peak 1) was also observed. The peak currents of peak 1 increased slightly as the fluoride concentration

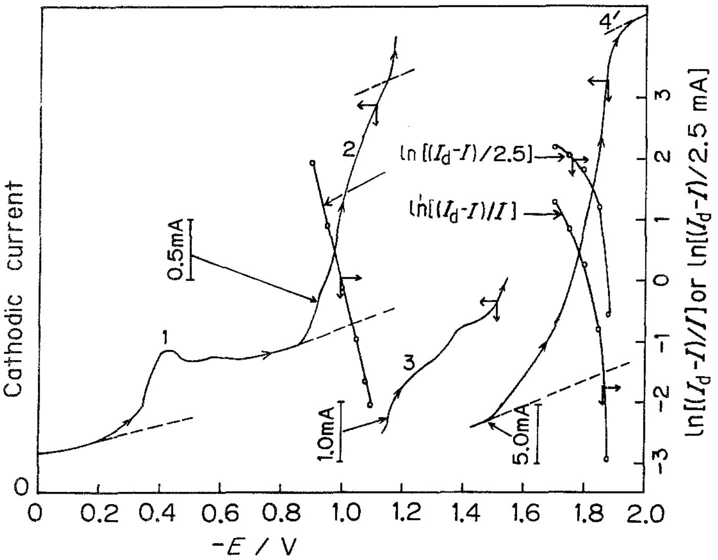

Fig. 3. The steady voltammogram of zirconium on platinum electrode (0.08 cm^2) in KCl–NaCl–4.76 wt % $ZrCl_4$ melts with 5.08 wt % KF($X_{F-}/X_{Zr4+} = 4.3$) at 973 K and the functions of $\ln[(I_d - I)/I]$ against potential. The scanning rate is 3.3 mV s^{-1}.

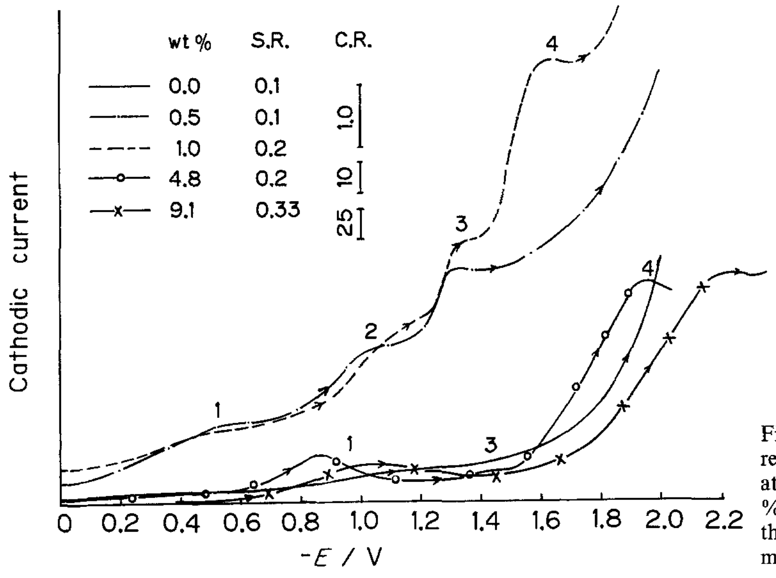

Fig. 4. The effects of K_2ZrF_6 concentrations on the reduction of zirconium in equimolar KCl–NaCl melts at 973 K on a platinum electrode (0.08 cm^2). Here, % wt represents the weight percent of K_2ZrF_6; S.R., the scanning rate (V s^{-1}); C.R., the current range in mA.

increased, but were much smaller than those at peak 4. Therefore, we can conclude that peak 4 represents the main reduction of zirconium when the ratio, $Z_{F^-}/X_{Zr^{4+}} \geqslant 6$.

When $0 < X_{F^-}/X_{Zr^{4+}} \leqslant 6$, peak 4 became broad as the ratio increased. This was probably due to the fact that peak 4 is associated with several reduction reactions. In this case, Equation 1 cannot be applied to estimate the electron number involving these reactions. However, peak 4 gradually grew sharp as the fluoride concentration increased when the ratio was larger than 6 (Figs. 2a and 2b). A very sharp reduction peak (Fig. 2b) was obtained when the ratio was 22. The electron number related to peak 4 in this case was estimated to be 3.84 according to Equation 1 ($E_{PC} - E_{PC/2} = -48$ mV).

The steady voltammogram of zirconium reduction in KCl–NaCl–4.76 wt % $ZrCl_4$ melts with 5.08 wt % $KF(X_{F^-}/X_{Zr^{4+}} = 4.3)$ and the plots of E against $\ln [(i_d - i)/i]$, where i_d is the limiting current, are represented in Fig. 3. A good linear plot with an n value of 1.69 from the slope ($RT/(nF)$, theoretically) of E against $\ln [(i_d - i)/i]$ was obtained for peak 2 ($ZrCl_6^{2-} + 2e^- \rightarrow ZrCl_6^{4-}$). However, the relations of E against $\ln [(i_d - i)/i]$ for soluble products and also $\ln [(i_d - i)/i]$ for peak 4 when the ratio was 22, was non-linear. This is probably because peak 4 is associated with several reduction reactions of $ZrCl_{6-x}F_x^{2-}$, where x is less than 6 and with several different values, or ZrF_7^{3-}. However, a good linear plot of E against $\ln [(i_d - i)/i]$ for peak 4 when the ratio was 22, was obtained, and the electron number was calculated to be approximately 4.1 from the slope (0.02045 V). Thus, the main reduction reaction in the chloride–fluoride bath in which $X_{F^-}/X_{Zr^{4+}} \geqslant 6$, can be reasonably suggested to proceed according to the following reaction.

$$ZrCl_{6-x}F_x^{2-} + 4e^- \longrightarrow Zr + (6 - x)Cl^- + xF^- \qquad (8)$$

where, the value of x in the complex ions will be discussed later in this paper.

The linear sweep voltammograms of zirconium in equimolar KCl–NaCl melts with various concentrations of K_2ZrF_6 are presented in Fig. 4. The voltammogram behaviour is dependent on concentration. Comparison of these results with those in KCl–NaCl–$ZrCl_4$ (Fig. 1), shows that the linear voltammogram in the melts with 0.5 wt % K_2ZrF_6 is very similar to that in chloride melts. Therefore, peaks 2 and 3 were due to zirconium chloride complex ($ZrCl_6^{2-}$) reduction reactions (reactions 2 and 3).

When the initial K_2ZrF_6 concentration increased to 1 wt %, a new well-defined peak (peak 4) appeared. It was observed that the peak potential (E_P) was independent of the scanning rates (0.1 V s^{-1} to 1 V s^{-1}) and equal to -1.6 V vs Ag/AgCl(0.1 M)–KCl–NaCl. The mean potential difference of peak to half peak at different scanning rates was -103 mV. According to Equation 1, an electron number value of 1.79 was obtained. For a steady voltammogram of zirconium in the melts with 1 wt % K_2ZrF_6, the plot of E against the function $\ln (i_d - i)/i]$ was linear with a slope, 42.17 mV close to the theoretical value 41.91 mV for a two-electron reversible process. From the results, this peak was considered to be due to the following reactions.

$$ZrCl_{6-x}F_x^{2-} + 2e^- \longrightarrow ZrCl_{6-x}F_x^{4-} \qquad (9)$$

$$ZrCl_{6-x}F_x^{4-} + 2e^- \longrightarrow Zr + (6 - x)Cl^- + xF^- \qquad (10)$$

which is similar to Zr reduction in the chloride bath. The peak due to reaction 9 probably existed between peaks 2 and 3 associated with the reduction of zirconium chloride.

When 2 wt % K_2ZrF_6 was added to the melts, peak 4 became a peak with a shoulder and a peak potential of -1.78 V was observed independent of the scanning rates (0.1 V s^{-1} to 1 V s^{-1}). Peak 4 given in Fig. 4, could not be separated, only a very broad peak was observed as K_2ZrF_6 concentration became more than 3 wt %. The higher the K_2ZrF_6 concentration (1 to 13 wt %), the less the peak potential shifted. Also, it is clear that peak 4 represented the main cathodic zir-

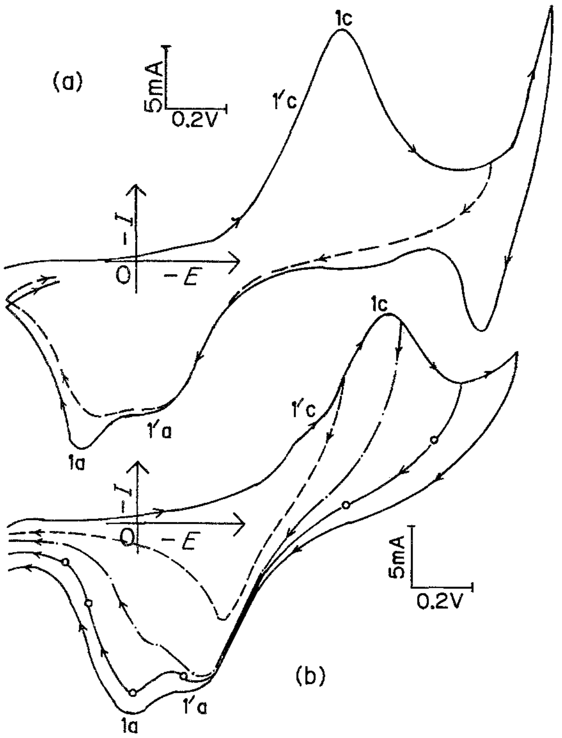

Fig. 5. Amplified cyclic voltammetry for peak 1 (Fig. 6) in KCl–NaCl melts with Zr^{4+} on a platinum electrode ($0.08\,cm^2$) at 973 K. (a), 3.54 wt % ZrF_4, $0.33\,V\,s^{-1}$; (b), 3.54 wt % ZrF_4 + 1.19 wt % KF, $0.1\,V\,s^{-1}$.

conium reduction process in the bath with higher concentration of K_2ZrF_6, although a small peak (peak 1) was observed.

Amplified cyclic voltammograms for peak 1 as shown in Figs 2 and 4 are presented in Fig. 5 to clarify the behaviour of the lower concentration zirconium complex ions (the main complex to be reduced in accordance with reaction 8) in the bath with higher fluoride concentration. The relations of the cyclic voltammograms and the switching potential are also given. Clearly, the anodic voltammograms are more complex than the cathodic ones. Peak 1'a on the anodic side was associated with the shoulder (peak 1'c) of the cathodic peak. As the switching potentials became less, peak 1a became more obvious. The peak potential difference of peak 1a to peak 1c is much larger than that of peak 1'a to peak 1'c. Thus, it can be concluded that this represents a charge transfer followed by a chemical reaction (EC). The products formed by the following chemical reaction were electro-oxidised with greater difficulty. The peak potential of peak 1c changed with the scanning rates as shown in Fig. 6. According to Nicholson [21], this could be due to a fast subsequent reaction, since a slow subsequent chemical reaction should not affect its charge transfer reaction.

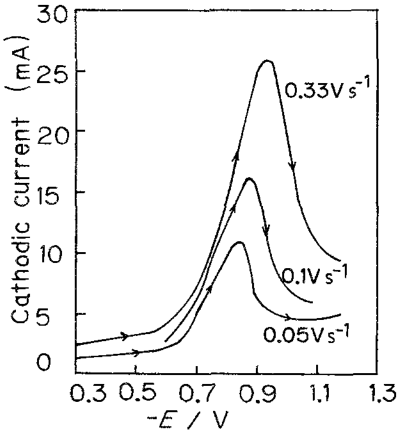

Fig. 6. The effects of scanning rate on the voltammogram of zirconium in KCl–NaCl–13.04% K_2ZrF_6 melts on a platinum electrode ($0.08\,cm^2$) at 973 K.

Linear relations between peak currents and the square roots of the scanning rates in the range, $0.1\,V\,s^{-1}$ to $1\,V\,s^{-1}$ (Fig. 7) implies that the reduction reaction is quasi-irreversible. Therefore, Equation 1 can be also approximately used for the estimation of the electron number of the charge transfer reaction for an EC process with a reversible charge transfer reaction. A mean n-value of 1.21 was obtained from Equation 1.

According to the results and discussion above, the proposed electrochemical reaction mechanism of zirconium in chloride–fluoride melts with less fluoride is a double two-electron reduction process, i.e., the electroreduction of zirconium in the bath with lower fluoride concentration is similar to the behaviour of zirconium ion reduction in a chloride molten bath with $ZrCl_4$. In the mixed bath with higher fluoride concentration, the main zirconium complex ions were directly reduced to metallic zirconium as shown in Reaction 8. From the results obtained in this work, it has been made clear that there also exist other zirconium chloride–fluoride complex ions reduced according to the following reactions

$$ZrCl_{6-x}F_x^{2-} + e^- \longrightarrow ZrCl_{6-x}F_x^{3-} \qquad (11)$$

$$ZrCl_{6-x}F_x^{3-} + 3e^- \longrightarrow Zr + (6-x)Cl^- + xF^- \qquad (12)$$

from consideration of the electron number of peak 1

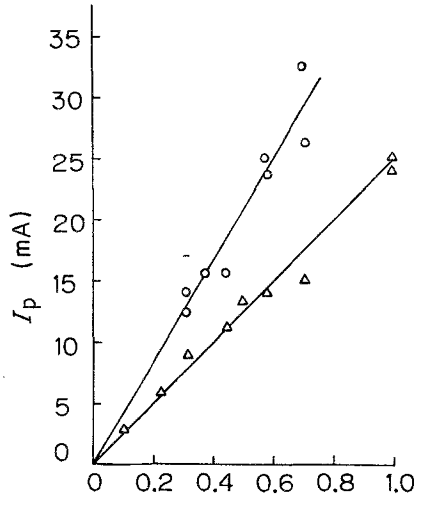

Fig. 7. Function of the first peak current of the electrochemical reduction of zirconium in KCl–NaCl molten salts with 5.81 wt % ZrF_4 (○) or 7.41 wt % K_2ZrF_6 (△) at 973 K. The surface area of the platinum electrode is $0.08\,cm^2$.

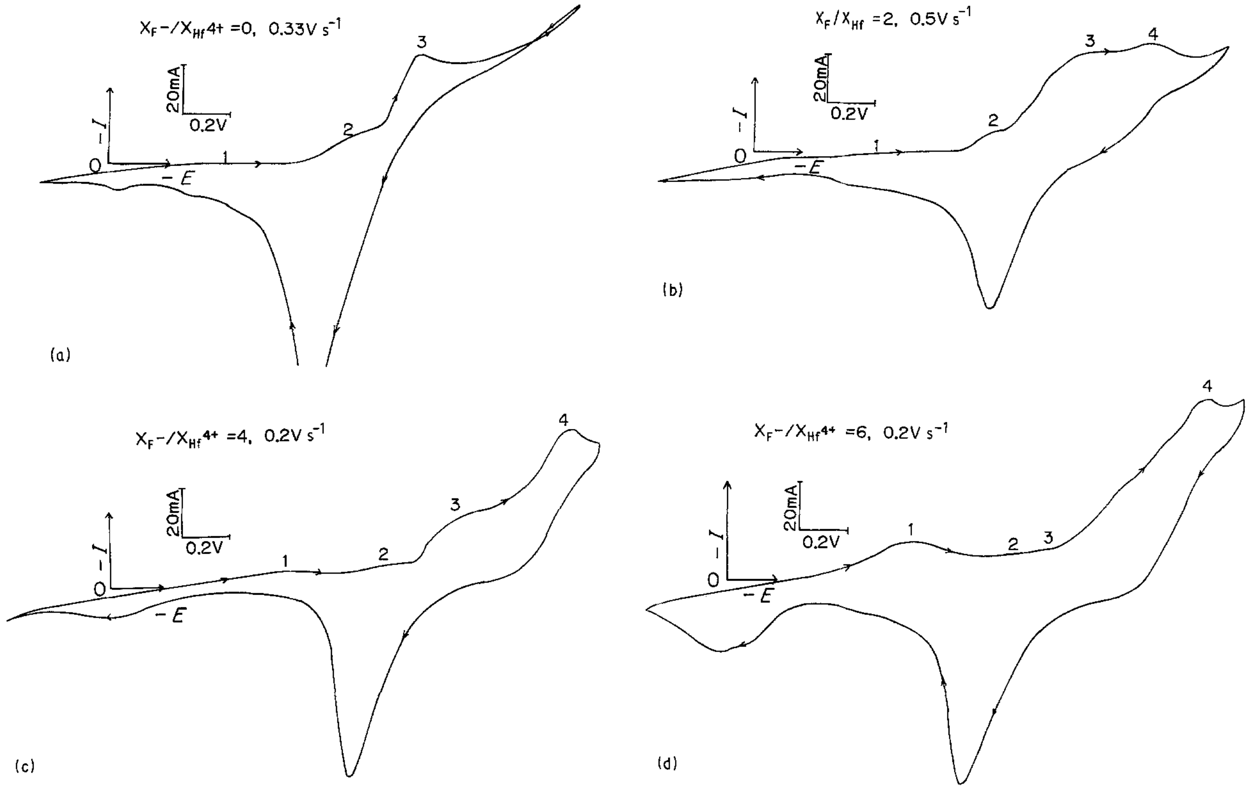

Fig. 8. Cyclic voltammograms of hafnium in KCl–NaCl molten salts with Hf^{4+} complex on a platinum electrode (0.08 cm^2) at 973 K. (a), 3.22 wt % $HfCl_4$; (b) 3.22 wt % $HfCl_4$ + 1.15 wt % KF; (c), 5.27 wt % ZrF_4; (d), 5.27 wt % HfF_4 + 2.34 wt % KF.

shown in Figs 2, 4 and 5 which was approximately equal to 1. Therefore, zirconium electroreduction in the molten bath was very complicated and dependent on the solute and the fluoride concentration. The fluoride compounds played a major role in the zirconium reduction behaviour. These results are different from those obtained in the literature [9, 12] in which the reduction of zirconium in chloride–fluoride mixed molten salts was simply considered to be Zr^{4+} (complex) + $4e^- \rightarrow$ Zr.

3.2. *Electrochemical studies of hafnium in the molten salts*

Typical cyclic voltammograms of hafnium in chloride and fluoride–chloride melts at 973 K on a platinum electrode are represented in Fig. 8. Comparison of the results in Fig. 8a with those for zirconium in equimolar KCl–NaCl melts with $ZrCl_4$ (Fig. 1) indicates that the cyclic behaviour of hafnium in KCl–NaCl melts with $HfCl_4$ are very similar to those of zirconium. Analysis of the cyclic voltammograms shows that both peak potentials 2 and 3 are independent of the scanning rates (0.1 V s^{-1} to 1 V s^{-1}). Therefore, the cathodic reactions are reversible. Plots of E against ln $[(i_d - i)/i]$ are linear for peak 2 and peak 3. The electron number of 1.89 and 2.30 for peak 2 and peak 3, respectively, was obtained from the slope. An n value of 2.04 for peak 3 is also determined by use of the potential difference between half peak to peak. A suggested double two-electron reduction process for the electroreduction of hafnium in chloride melts proceeds as follows

$$Hf^{4+} \text{ (chloride complex)} + 2e^- \longrightarrow Hf^{2+} \text{ (chloride complex)} \qquad (13)$$

$$Hf^{2+} \text{ (chloride complex)} + 2e^- \longrightarrow Hf \qquad (14)$$

This is different from data in the literature [15].

The different cyclic voltammograms of hafnium in the chloride-fluoride mixed bath are demonstrated in Fig. 8b to d to elucidate the effects of fluoride ions on the electrochemical behaviour. As the mole fraction ratio, $X_{F^-}/X_{Hf^{4+}}$ (where X_{F^-} is the mole fraction of F^- ions and $X_{Hf^{4+}}$ is the mole fraction of Zr^{4+} complex ions), increased, the peak currents associated with the reduction of hafnium chloride complex ($HfCl_6^{2-}$) decreased. When the ratio was 2, a new peak (peak 4) became clear. The peak currents related to peak 4 increased significantly as more KF was added to the bath. Peak 4 also became a very broad cathodic peak in the ratio range $0 < X_{F^-}/X_{Hf^{4+}} \leqslant 6$. However, in the case of the ratio larger than 6, the peak width of peak 4 gradually became sharp with the fluoride ratio increase. A very sharp peak (peak 4) was observed as the fluoride ratio became larger than 16. An n value of 4.1 involved in the peak was determined from the potential difference (45 mV) of half peak to peak. Also, a small peak can be detected in the bath with higher fluoride concentrations as depicted in Fig. 8(c) and d. This behaviour is very similar to that of zirconium.

Amplified cyclic voltammograms of peak 1 as shown in Fig. 8 are depicted in Fig. 9. A well-defined cathodic peak was observed. However, the reverse anodic voltammograms were complicated and two

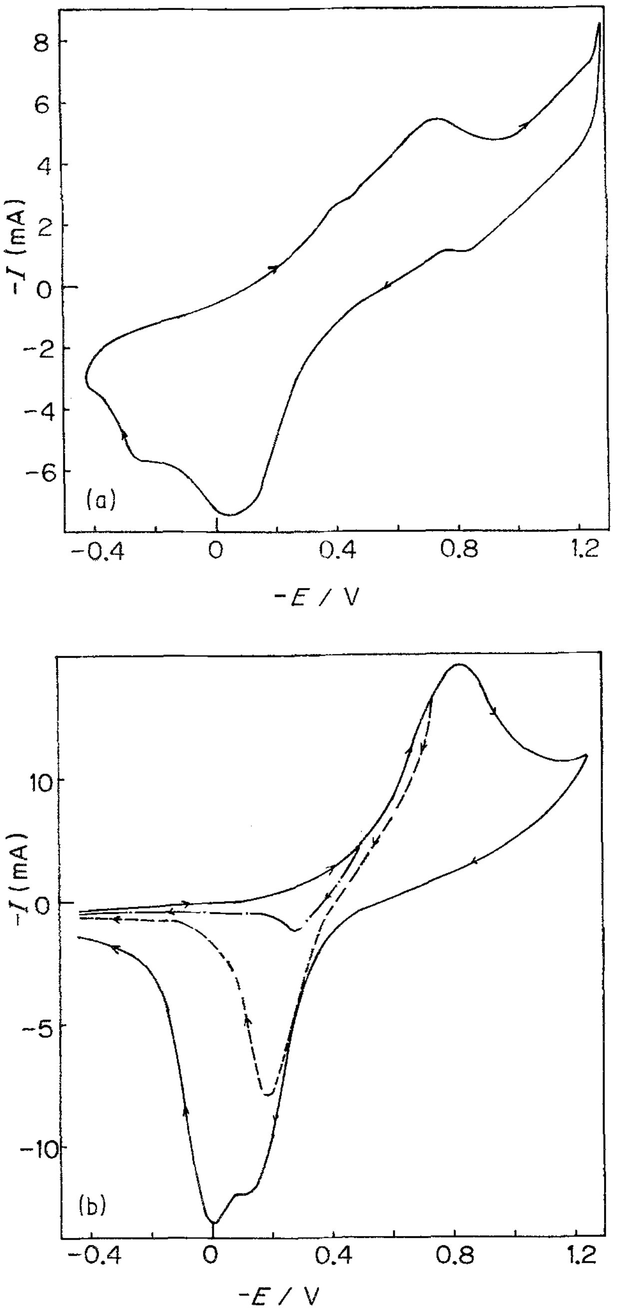

Fig. 9. Amplified voltammogram of the first peak of hafnium reduction on a platinum electrode ($0.08\,cm^2$) at 973 K. (a) 5.27 wt % HfF_4, sweep rate $0.33\,V\,s^{-1}$; (b) 5.27 wt % HfF_4 + 2.34 wt % KF, sweep rate $0.14\,V\,s^{-1}$.

peaks were observed. The cathodic peak potentials changed with scanning rate and shifted to lower potential as the scanning rate increased, but, the two-anodic peak potentials were independent of the scanning rate. It can be reasonably assumed that the reduction of hafnium in chloride–fluoride melts is also a charge transfer followed by a chemical reaction which is similar to the case of zirconium in section 3.1.

Fig. 10 shows that the cathodic peak currents of peak 1 are approximately proportional to the square root of the scanning rate in the range $0.1\,V\,s^{-1}$ to $0.5\,V\,s^{-1}$. Thus the cathodic charge transfer reaction is reversible. The mean potential difference of peak to half-peak, − 193 mV, was used to estimate the electron number. An n value of 0.96 was calculated from Equation 1.

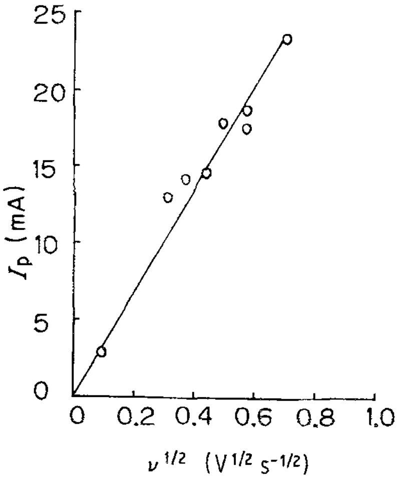

Fig. 10. The relation between the scanning rate and the first peak current of hafnium reduction on a platinum electrode ($0.08\,cm^2$) at 973 K in KCl-NaCl molten salts with 5.27 wt % HfF_4 + 2.34 wt % KF.

The reduction process in the mixed bath with lower fluoride is similar to that of the chloride molten salts with $HfCl_4$ as given by reactions 13 and 14. In the bath with higher fluoride compounds, the main hafnium complex ions were cathodically reduced according to the following reaction

$$HfCl_{6-x}F_x^{2-} + 4e^- \longrightarrow Hf + (6-x)Cl^- + xF^- \qquad (15)$$

However, the other lower concentration hafnium complex ions were considered to reduce as

$$HfCl_{6-x}F_x^{2-} + e^- \longrightarrow HfCl_{6-x}F_x^{3-} \qquad (16)$$

$$HfCl_{6-x}F_x^{3-} + 3e^- \longrightarrow Hf + (6-x)Cl^- + xF^- \qquad (17)$$

This mechanism is similar to that of zirconium in the bath as shown in section 3.1. Hafnium chloride complex ions gradually change into fluoride–chloride complex or fluoride complex ions as the fluoride composition increases. A more stable hafnium complex ion is formed in the bath with higher concentrations of fluoride compounds.

4. Effects of fluoride ions on the cathodic reduction potential of zirconium and hafnium in the mixed molten bath

As discussed above, the electrochemical behaviour of zirconium and hafnium in chloride–fluoride molten salts were markedly dependent on fluoride composition. In this section, the effects of the fluoride compounds on the reduction potentials and zirconium (hafnium) complex ions are discussed in more detail.

Fig. 11 shows the relations between $\Delta E_{3/4}$ and ln (X_{F^-}), where, $\Delta E_{3/4}$ is the difference of $E_{3/4}$ of $Zr^{4+}(Hf^{4+}) \rightarrow Zr(Hf)$ in chloride–fluoride molten salts and $E_{3/4}$ in chloride mixed molten salts; $E_{3/4}$ is the potential at $I = (3/4)I_p$ for peak 4 as shown in Figs 2 and 8 and is approximately equal to $E_{1/2}$; X_{F^-} is the apparent mole concentrations of fluoride ions in

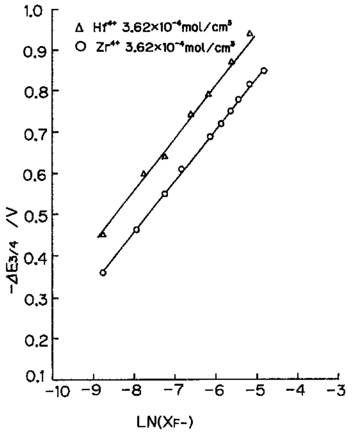

Fig. 11. Plots of $\Delta E_{3/4}$ ($= E_{3/4}$ (of zirconium or hafnium in chloride–fluoride melts $-$ $E_{3/4}$ (in chloride molten salts)) against $\ln(X_{F^-})$. Here $\Delta E_{3/4}$ is the mean value at various scanning rates; temperature: 973 K; platinum electrode: 0.08 cm^2.

mol cm^{-3}. It is evident that the cathodic reduction potentials shifted to lower values with increase of the fluoride concentration. Also, the potentials of $Hf^{4+} \rightarrow Hf$ were more negative than those of $Zr^{4+} \rightarrow Zr$.

Kipouros *et al.* [5–6] pointed out that the main zirconium (hafnium) complex ions in alkali chloride molten salts exist as $ZrCl_6^{2-}$($HfCl_6^{2-}$) ions. In this study, it can be considered that there exists an equilibrium between $ZrCl_6^{2-}$($HfCl_6^{2-}$) and $ZrCl_{6-x}F_x^{2-}$ ($HfCl_{6-x}F_x^{2-}$) with addition of fluorides (KF or NaF) to the chloride bath according to the following two reactions:

$$ZrCl_6^{2-} + xF^- = ZrCl_{6-x}F_x^{2-} + xCl^- \quad (18)$$

$$HfCl_6^{2-} + xF^- = HfCl_{6-x}F_x^{2-} + xCl^- \quad (19)$$

The x values may change with the fluoride concentration in the bath. The determination of x values will be pursued in future work. From the results given in Fig. 11, it can be concluded that the complex $HfCl_{6-x}F_x^{2-}$ is more stable than $ZrCl_{6-x}F_x^{2-}$. Hafnium ions in chloride–fluoride bath with zirconium ions and hafnium ions should more easily change from chloride complex ions to fluoride complex ions than zirconium ions.

5. Conclusion

According to the experimental data obtained by the use of linear and cyclic voltammograms, it is proposed that the electrochemical reduction of zirconium and hafnium on platinum electrodes in chloride or fluoride–chloride melts occurs by a different mechanism for low and high bath concentrations of fluoride. The electrochemical reduction of zirconium in chloride or fluoride–chloride with lower fluoride composition is considered to proceed according to Zr^{4+} (complex) + $2e^- \rightarrow Zr^{2+}$ (complex), Zr^{2+} (complex) + $2e^- \rightarrow Zr$. However, it is suggested that the reduction of zirconium in the bath with the higher concentration of fluoride takes place directly from Zr^{4+} (complex) to metallic Zr. A similar reduction process for hafnium is also proposed. It was observed that hafnium fluoride complex ions were more stable than zirconium fluoride ions.

References

[1] I. N. Sheiko, T. N. Grechina and V. T. Barchuk, *Ukr. Khim. Zh.* **30** (1964) 1055.
[2] T. Sakakura and T. Kirihara, *Denkikagaku* **36** (1968) 109.
[3] T. Sakakura and T. Kirihara, *Denkikagaku* **38** (1970) 496.
[4] D. A. Asvestas, P. Pint, and S. N. Flengas, *Can. J. Chem.* **55** (1977) 1154.
[5] G. J. Kipouros and S. N. Flengas, *ibid.* **56** (1978) 1549; **59** (1981) 990.
[6] G. J. Kipouros and S. N. Flengas, *ibid.* **61** (1983) 2183.
[7] F. Basile, E. Chassaing, and G. Lorthioir, *J. Applied Electrochem.* **11** (1981) 645.
[8] G. J. Kipouros and S. N. Flengas, *J. Electrochem. Soc.* **132** (1985) 1087.
[9] L. P. Polyakova and P. T. Stangrit, *Electrochimica Acta* **27** (1982) 1641.
[10] M. V. Smirnov, A. N. Baraboshkin and V. E. Komarnov, *J. Chem. Phys.* **37** (1963) 1669.
[11] C. Eon , C. Pomimier and J. G. Fondanaiche, *Bull. Soc. Chim. Fr.* **7** (1969) 2574.
[12] R. Winand, *Electrochimica Acta* **7** (1962) 475; **8** (1963) 53.
[13] I. N. Sheiko and V. G. Fechenko, *Ukr. Khim. Zh.* **25** (1959) 166.
[14] I. N. Sheiko, A. V. Gorodyskii, and M. I. Bykova, *Zh. Neorg. Khim.* **6** (1961) 2341.
[15] T. Sakakura and T. Kirihara, *Denkikagaku,* **37** (1969) 107.
[16] C. Guang-sen, M. Okido and T. Oki, *J. Applied Electrochem.* **17** (1987) 849.
[17] C. Guang-sen, M. Okida and T. Oki, *ibid.*, to be published.
[18] C. Guang-sen, M. Okida and T. Oki, *Electrochimica Acta* **32** (1987) 1637.
[19] T. Oki, M. Okida and C. Guang-sen, Proceedings of The Joint International Symposium on Molten Salts, The Electrochemical Society In., (1987) p. 507.
[20] C. Guang-sen, M. Okida and T. Oki, to be published.
[21] R. S. Nicholson and I. Shain, *Anal. Chem.* **36** (1964) 706.
[22] I. N. Shieko, *Ukr. Khim. Zh.* **29** (1963) 727.