

Insights into the Electrochemistry of the Deposition of Boron from KCl-KF-NaBF₄ Melt

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Abstract

Electrochemical reduction of boron from boron containing fluoroborate species present in KCl (81.54 mol%)-KF (18.45 mol%)-NaBF₄ (1.67x10⁻⁴ mol cm⁻⁴) melt on a platinum electrode was studied by cyclic voltammetry and chronoamperometry. These studies were carried out over the temperature range 1073 – 1123 K. Boron-containing electroactive species is shown to reduce quasi-reversibly at low scan rates ($v < 0.1 \text{ Vs}^{-1}$) and irreversibly at higher scan rates ($> 0.1 \text{ V s}^{-1}$) through a single-step three-electron process (B(III) + 3e → B). The transfer and diffusion coefficients of the electroactive species were measured for sodium fluoroborate in KCl-KF melt over the temperature range 1073 – 1123 K.

Keywords: Sodium fluoroborate; Cyclic voltammetry; Chronoamperometry; Diffusion coefficient; Melt.

Introduction

Boron carbide containing boron enriched in ¹⁰B isotope (67 at.%) will be used in the control rods of the Indian Prototype Fast Breeder Reactor (PFBR) [1]. An indigenous process developed for fabricating high-density boron carbide pellets for this application envisages the synthesis of boron carbide from enriched boron by reacting it with carbon [2]. A high temperature (1073 K) molten salt electrolysis process was developed for the synthesis of high purity boron [3 - 5] suitable for control rod application in fast reactors. The electrolyte employed is a melt comprising KCl (72.96 mol %), KBF₄ (11.04 mol %) and KF (16 mol %)

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[3]. In order to have a more fundamental insight into the process with different melt compositions, a detailed experimental programme is currently being pursued at the Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam, India. The electrochemistry of KCl-KF-KBF₄ (1.6×10^{-4} to 7.73×10^{-4}) melts has been reported in our previous study [5]. A systematic study on boron deposition from other alkali metal fluoroborates in KCl-KF melt has not been reported yet. The electrochemistry of boron is being studied since 1925 due to its nuclear and non-nuclear industrial applications [6 - 9]. Researchers have studied electrodeposition of elemental boron from various boron containing melts [10 - 22]. In this context fluoroborate containing melts have been extensively studied [23 - 30]. The reduction of B(III) in NaCl-KCl-MBF₄ (M = Na and K) melts was studied by Taranenko *et al.* [25]. The concentration of MBF₄ in these melts varied from 3×10^{-5} to 8×10^{-4} mol cm⁻³. The voltammograms were recorded on a glassy carbon electrode at 973 K. The reduction potential of B from B(III), with respect to an Ag/AgCl reference electrode, involving a single-step three-electron transfer process, was reported by these authors. The decrease in concentration of the electrochemically active species in the melt with time was reported to be due to chemical reaction of tetrafluoroborate with the chloride melt and (or) by the thermal decomposition of tetrafluoroborate. According to Danek *et al.* [31], the dissolution of KBF₄ in MCl (M= Li, Na, K) melts was proposed to follow the following exchange reactions:



The KBCl₄ thus formed decomposes according to Eqn. (2).



The stability of BF₄⁻ anions in molten alkali chlorides was reported to increase as LiCl < NaCl < KCl due to the strong polarizing effect of the cation (Li⁺ > Na⁺ > K⁺) [25]. Decomposition of BCl₄⁻ ions was not observed in NaCl and KCl melt system. It was assumed that MBF₄ thermally decomposed to gaseous BF₃ according to Eq. (3).



Thermodynamic analysis substantiated that the addition of F⁻ ions to the chloride melts shifted the equilibrium of Eqns. (1) and (3) to the left and consequently suppressed the decomposition of the electrochemically active species. Thus chloride-fluoride supporting electrolyte was better suited compared to pure chloride melts for the electrodeposition of boron.

The aim of the present work is to investigate the electrochemical reduction of boron containing electroactive species in KCl-KF-NaBF₄ melt and evaluate the kinetic parameters of the electroreduction process. Transient electrochemical techniques such as cyclic voltammetry and chronoamperometry have been used in the present study.

Experimental

Materials

KCl (99.5 % purity) and KF (99 % purity) were supplied by M/s. Loba Chemie Pvt. Ltd., Mumbai, India. NaBF₄ (> 98% purity) was obtained from M/s. Sigma Aldrich, USA. High-density (1.85 g cm⁻³) graphite was procured from M/s. Pure Components Pvt. Ltd., Pondicherry, India. Platinum wire (1 mm dia, 99.99% purity) was procured from M/s. Sevantilal Mahasukhlal, Mumbai, India. Inconel 600 (99.9% purity) which formed the structural material of the electrochemical cell was supplied by M/s. Kalapura Engineering, Mumbai, India.

Electrochemical studies

Voltammetric studies were carried out over the temperature range 1073 – 1123 K. The electrochemical cell described elsewhere [5] was operated under argon during the measurement. The experiments were conducted using a three-electrode assembly. A high-density graphite crucible served as the container for the electrolyte as well as the auxiliary electrode. Platinum wire (1 mm diameter) served as the working electrode. The surface area of the Pt electrode dipped in the electrolyte was kept constant at 0.23 cm² for each measurement. The potentials were measured against an Ag/AgCl reference electrode developed in our laboratory [32]. The voltammograms were measured using the electrochemical workstation Autolab (PGSTAT 302N) equipped with an IF 030 interface.

Chronoamperometric studies

Chronoamperometric measurements were carried out employing a platinum electrode (0.23 cm² area) by applying potentials ranging from -0.88 to -0.85 V for a short duration of 5 s for the KCl (81.54 mol%)-KF (18.45 mol%) melt with NaBF₄ (1.67x10⁻⁴ mol cm⁻³) over the temperature range 1073 – 1123 K. Chronoamperograms were also measured using an Autolab (PGSTAT 302N) equipped with an IF 030 interface.

Analysis of boron in the melt

After the completion of the voltammetric scans, melt samples were withdrawn from the cell and analyzed. About 10 mg of the solidified melt were dissolved in 10 mL of 0.02 N HNO₃. The solution was then analyzed for its boron content by inductively coupled plasma mass spectrometer (ICP-MS, Model: Elan 250, M/s. Sciex, Toronto, Canada) after suitable dilution. These measurements had a standard deviation of about 3 to 5% of the reported value.

Results and discussion

Cyclic voltammetry

The cyclic voltammograms (CV) of the melt KCl (81.54 mol%)-KF (18.45 mol%)-NaBF₄ (1.67x10⁻⁴ mol cm⁻³) (designated as melt A) were recorded over the temperature range 1073 – 1123 K. Typical cyclic voltammograms of this melt

at various scan rates ($0.05 - 2.0 \text{ V s}^{-1}$) are shown in Fig. 1. It is seen that the cathodic peak shifts to a more negative potential and the anodic peak shifts to a more positive potential with increasing scan rates. In addition, the peak current increases with increase in scan rate.

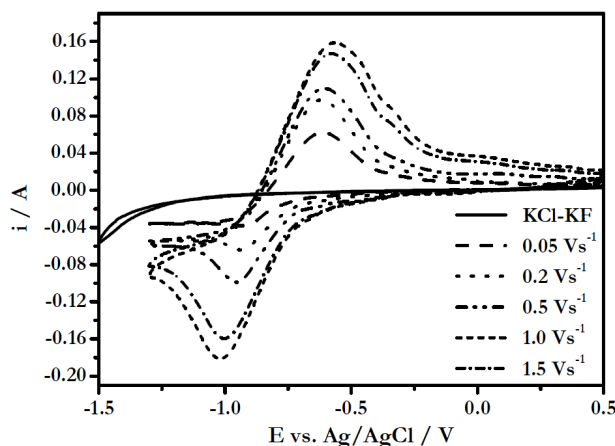


Figure 1. Cyclic voltammetric scans of the melt A on Pt electrode with varying scan rates at 1073 K.

Fig. 2 shows the CVs of the melt A at 1073, 1098 and 1123 K. The cathodic (E_p^C) and anodic (E_p^A) peak potentials of the electroactive species as well as the average of the cathodic and anodic peak potentials, $(E_p^C + E_p^A)/2$, of this melt at different temperatures are given in Table 1. It is observed that the cathodic and anodic peak potentials are shifted to less negative values (Fig. 2) and the average values increase with increase in temperature (Table 1). It is also observed that the magnitude of $E_{P/2}^C - E_p^C$, ($E_{P/2}^C$ is cathodic half-peak potential), is larger than the value required for the reversible process of formation of an insoluble substance ($0.071/n$)V at 1073 K where, n is the number of electrons transferred for the reduction process) [33, 34] indicating that the reduction of boron species on platinum electrode from KCl-KF- NaBF_4 melt is not reversible.

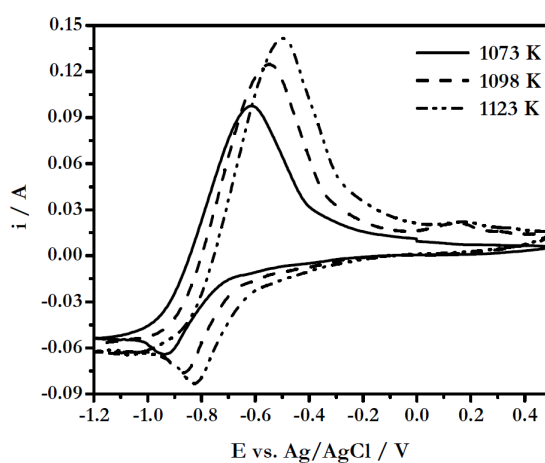


Figure 2. Cyclic voltammetric scans of the melt A on Pt electrode at different temperatures (scan rate: 0.2 V s^{-1}).

Table 1. Electrokinetic parameters calculated for the electroactive species in the melt A employing the platinum electrode.

T (K)	Scan rate (v/V s ⁻¹)	Cathodic peak potential (E _P ^C /V)	Anodic peak potential (E _P ^A /V)	(E _P ^C +E _P ^A)/2 (V)	E _{P/2} ^C - E _P ^C (V)	α from Eqn. 4	α from Eqn. 5
1073	0.1	-0.927	-0.614	-0.770	0.094	0.60	
	0.5	-0.955	-0.608	-0.781	0.118	0.48	
	1.0	-0.975	-0.590	-0.782	0.133	0.43	
	2.0	-1.018	-0.565	-0.791	0.160	0.36	0.34
1098	0.1	-0.854	-0.549	-0.701	0.083	0.69	
	0.5	-0.894	-0.554	-0.724	0.106	0.54	
	1.0	-0.925	-0.542	-0.733	0.125	0.46	
	2.0	-0.971	-0.517	-0.744	0.152	0.37	0.34
1123	0.1	-0.786	-0.493	-0.639	0.089	0.64	
	0.5	-0.802	-0.432	-0.617	0.109	0.52	
	1.0	-0.833	-0.426	-0.629	0.125	0.46	
	2.0	-0.879	-0.394	-0.636	0.149	0.38	0.31

The reduction potential of boron from boron containing electroactive species in the melt A was found to be more negative compared to that of melt KCl (81.54 mol%)-KF (18.45 mol%)-KBF₄ (1.6x10⁻⁴ mol cm⁻³) (designated as melt B) [5] (Fig. 3).

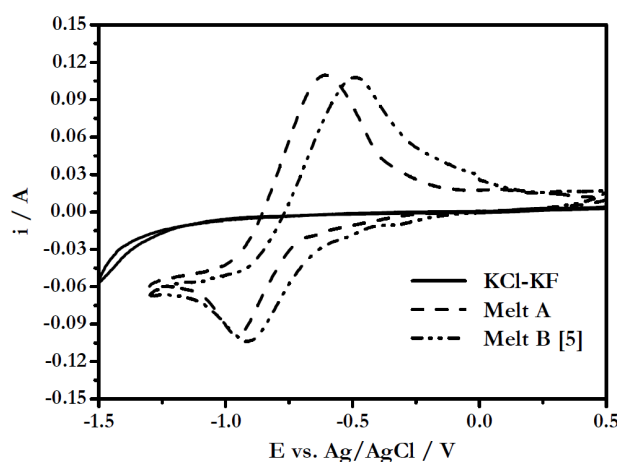
**Figure 3.** Cyclic voltammetric scans of the melts A and B on Pt electrode at 1073 K and 0.5 V s⁻¹ scan rate.

Fig. 4 shows the plot of $i_p^C / \nu^{1/2}$ vs. $\nu^{1/2}$ where, i_p^C is the cathodic peak current and ν is the scan rate. It is observed from these plots that for the melt A at 1073 K, the $i_p^C / \nu^{1/2}$ values remain almost constant at polarization rate range of 0.05 to 2 V s⁻¹. This suggests that the process of electrodeposition of boron on Pt electrode is not complicated by chemical reactions as suggested by Tsiklauri *et al.* [35, 36]. In addition the electrodeposit is not adsorbed at the electrode surface. A similar behaviour was observed for the melts NaCl-KCl-KBF₄ [24] and melt B [5]. Thus it can be inferred that the electrodeposition of boron from alkali metal fluoroborate containing KCl-KF melts is not complicated by chemical reactions. The variation of E_p^C with the logarithm of scan rate, $\log \nu$, at different temperatures for melt A is shown in Fig. 5. As seen from the figure, the cathodic

peak potential varies linearly with $\log v$. These observations indicate that the reduction of electroactive boron species on platinum electrode is quasi-reversible at low scan rates ($v < 0.1 \text{ Vs}^{-1}$) and irreversible at higher scan rates ($> 0.1 \text{ V s}^{-1}$).

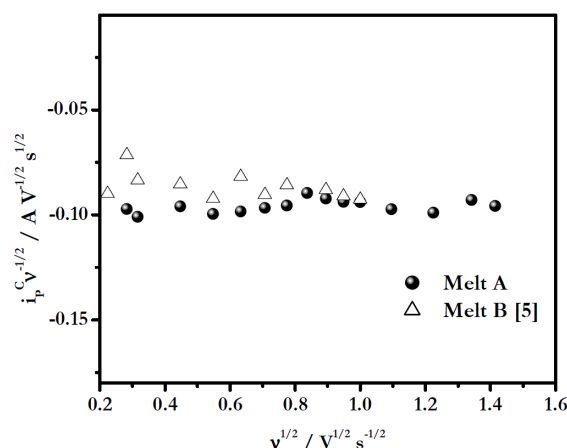


Figure 4. Plot of $i_p^C / v^{1/2}$ vs. $v^{1/2}$ for the melts A and B at 1073 K.

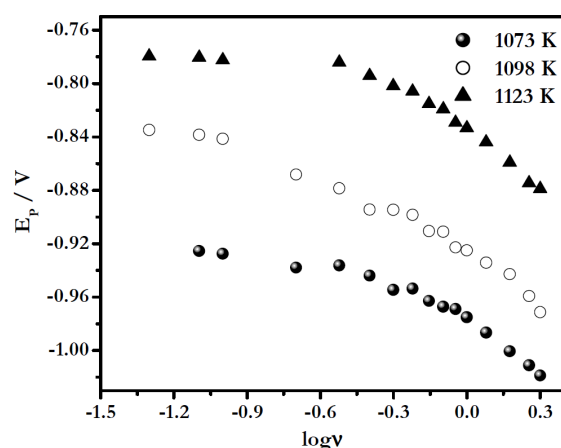


Figure 5. Cathodic peak potential versus logarithm of scan rate measured at different temperatures on a Pt electrode in the melt A.

The variation of the cathodic peak current, i_p^C , with the square root of scan rate, $v^{1/2}$, at different temperatures for the melt A is shown in Fig. 6. The linear relationship between i_p^C and $v^{1/2}$, as observed from these figures indicates that the process is diffusion controlled.

Calculation of transfer coefficient

The value of αn_α (where α is the transfer coefficient and n_α is the number of electrons transferred for the reduction process in the rate determining step) can be determined from the equation given by Matsuda and Ayabe (Eqn. 4) [37, 38].

$$E_{P/2}^C - E_P^C = \frac{1.857RT}{\alpha n_\alpha F} \quad (4)$$

where, R is the molar gas constant, T is the absolute temperature and F is the Faraday constant.

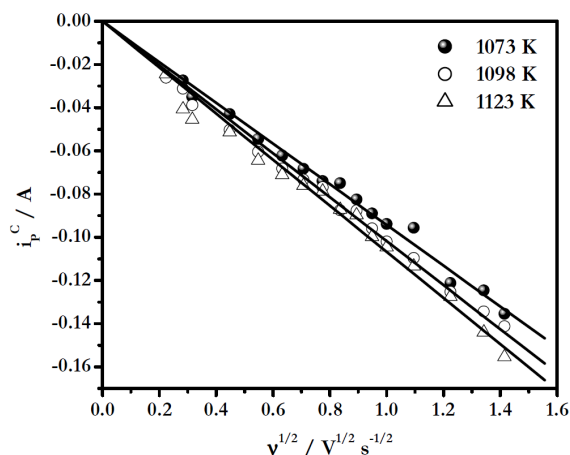


Figure 6. Cathodic peak current versus square root of scan rate at different temperatures on a Pt electrode in the melt A.

The αn_{α} also can be evaluated from the following equation [33].

$$\frac{\Delta E_p^C}{\Delta \log v} = \frac{2.3RT}{2\alpha n_{\alpha}F} \quad (5)$$

where $\frac{\Delta E_p^C}{\Delta \log v}$ is determined from the slope of E_p^C vs. $\log v$ plots.

The transfer coefficients calculated from Eqns. (4) and (5) for the melt A are given in Table 1. For the melt A at 1073, 1098 and 1123 K the transfer coefficients were found to vary from 0.60 – 0.36, 0.37 – 0.69 and 0.64 – 0.38, respectively. By using Eqn. (5) the transfer coefficients for the melt A were found to vary from 0.34 – 0.31. The typical transfer coefficient values signify that the process is irreversible. Similar inference has also been drawn for the melt B reported in our previous study [5].

Diffusion coefficients

The diffusion coefficient of the electroactive species can be measured by chronoamperometry using Cottrell equation (Eqn. (6)) [33].

$$i = \frac{nFAD_o^{1/2}C_o^*}{\pi^{1/2}t^{1/2}} \quad (6)$$

where A is the electrode area in cm^2 , C_o^* is the concentration of B(III) ion in mol cm^{-3} , D_o is the diffusion coefficient in $\text{cm}^2 \text{s}^{-1}$, F is the Faraday constant, i is the current in amperes and t is the transition time in s. Typical chronoamperograms of the melt A employing Pt electrode are shown in Fig. 7. A linear variation of i with $t^{-1/2}$ is observed as shown in Fig. 7(a).

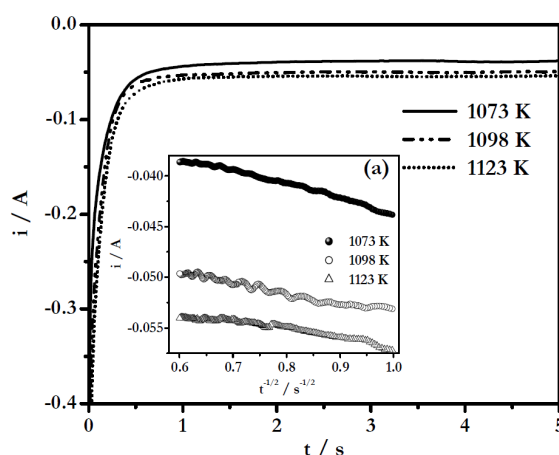


Figure 7. Chronoamperograms of the melt A on a Pt electrode (0.23 cm^2 area) carried out at -0.85 V potential scan. The inset (Fig. 7(a)) shows the plot of i vs. $t^{-1/2}$.

This indicates that the reduction of boron containing electroactive species in these melts is diffusion controlled. The diffusion coefficients of the electroactive species in the melt A were found to be $6.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 1073 K (Table 2). Also, typical diffusion coefficient values for different alkali metal fluoroborate containing melt system at different temperatures are presented in Table 2.

Table 2. Diffusion coefficient and electron transfer rate constant of the electroactive species in KCl-KF melts containing different fluoroborates at different temperatures.

Melt	Temperature (K)	Diffusion coefficient ($D_0 \times 10^6 / \text{cm}^2 \text{ s}^{-1}$)	Electron transfer rate constant ($k_s \times 10^3 / \text{cm s}^{-1}$)
A	1073	6.4	2.0
	1098	7.3	1.8
	1123	8.9	1.8
B [5]	1073	12	3.9
	1098	13	3.4
	1123	17	4.8

A comparative study of D_0 values of the boron containing electroactive species from different alkali metal fluoroborates in KCl-KF melt shows that $D_0^{\text{NaBF}_4} < D_0^{\text{KBF}_4}$. According to Stokes-Einstein equation (Eqn. (7)), the diffusion coefficient of a species is inversely proportional to its solvodynamic radius (r_s).

$$D_0 = \frac{kT}{C\pi\eta r_s} \quad (7)$$

where k is the Boltzmann constant, C is a constant and η is the absolute or bulk viscosity of the solvent. It is surmised that the solvodynamic radius (r_s) of the boron containing electroactive species varies as $r_s^{\text{NaBF}_4} > r_s^{\text{KBF}_4}$ in KCl-KF melt containing different alkali metal fluoroborates.

Electron transfer rate constant

Klingler and Kochi [39] derived an expression (Eqn. (8)) for obtaining the electron transfer rate constant (k_s) by assuming that the electron-transfer reaction is irreversible.

$$k_s = 2.18(\alpha n_\alpha)^{1/2} \left(\frac{D_o F V}{RT} \right)^{1/2} e^{\frac{\alpha^2 n F (E_p^C - E_p^A)}{RT}} \quad (8)$$

By using the above equation the electron transfer rate constants for the irreversible electrode process for sodium fluoroborate in KCl-KF melt over the temperature range 1073 to 1123 K were calculated. The k_s values obtained by substituting the αn_α values derived from Eqn. (4) at 1 V s⁻¹ scan rate and D_o from Eqn. (6) are presented in Table 2. These values indicate sluggish electron transfer kinetics due to the fact that the oxidized boron (fluoro-chloro complex of boron) and the reduced boron (elemental boron) are structurally dissimilar and the activation barrier for the redox process is large.

Apparent surface resistance

Polyakova *et al.* [34] reported that the broadening of the cathodic peak in CV occurred due to the ohmic control of deposition of boron. These authors presented linear plots of peak current and peak potentials against the square root of scan rate and concluded that a surface boron film formed on the electrode rendered the process to be controlled by ohmic resistance.

Table 3. Apparent surface resistance of the electrolyte on the platinum electrode for melts A and B at different temperatures.

Melt	Temperature (K)	R_{app} ($\Omega \text{ cm}^2$)
A	1073	0.21 ± 0.01
	1123	0.24 ± 0.01
B [5]	1073	0.18 ± 0.02
	1123	0.21 ± 0.01

The “apparent surface resistance” (R_{app}) of the electrolyte in the pores of the boron film covering the electrode can be obtained from the reciprocal of the slope of peak current density (j_p) vs. peak potential (E_p) plots, as reported by Polyakova *et al.* [34]. The plots for cathodic peak current density vs. cathodic peak potential for the melt A show a linear behavior. The values of R_{app} calculated for different fluoroborates in KCl-KF melt at different temperatures are presented in Table 3. It is observed (Table 3) that the R_{app} values decrease with increase in temperature. Polyakova *et al.* [34] reported a higher value of R_{app} (3.3 $\Omega \text{ cm}^2$ at 973 K) in the melt LiF-NaF-KF-KBF₄ (15.9x10⁻² mol%). In our earlier study on the melt B, the R_{app} (0.18 ± 0.02 $\Omega \text{ cm}^2$ at 1073 K) was found to be of similar magnitude [5]. Thus R_{app} was found to be independent of the nature of alkali metal fluoroborate in KCl-KF melt. The typical resistance values obtained (Table 3) in our present study are very small and it is surmised

that the effect of resistance on CVs is negligible and it does not quite affect the determination of α values from the cyclic voltammetric scans.

Conclusions

The electrochemical reduction of $B(\text{III}) + 3e \rightarrow B$ in KCl (81.54 mol%)-KF (18.45 mol%)- NaBF_4 (1.67×10^{-4} mol cm^{-3}) melt on a Pt electrode was studied by cyclic voltammetry over the temperature range 1073 to 1123 K. It is inferred that at a sweep rate of $v < 0.1 \text{ Vs}^{-1}$ the electroreduction is quasireversible and at $v > 0.1 \text{ Vs}^{-1}$, both the diffusion of electroactive species and the electron transfer play a role in the reduction process. It is established that the reduction of B(III) to B occurs by a single-step three-electron process. Using chronoamperometry, the diffusion coefficients of the boron containing electroactive species (B(III)) were calculated for the sodium fluoroborate melt system and it was found that $D_0^{\text{NaBF}_4} < D_0^{\text{KBF}_4}$. The values of α and R_{app} were found to be independent of the nature of alkali metal fluoroborate in KCl-KF melt.

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