

Exchange Current Measurements on the Nickel-Nickel(II)
Couple in Molten Fluorides*

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We have been concerned with the development of a practical reference electrode for molten fluoride compositions of importance in nuclear technology.⁽¹⁾ In the course of this work it became desirable to obtain an additional quantitative measure of the reversibility of the electrode process $\text{Ni(II)} + 2e \rightleftharpoons \text{Ni}$. It was decided to use one of the relaxation methods,⁽²⁾ since a fast charge-transfer was expected on the basis of available data on electrode kinetics in other molten salt solvents.⁽³⁾ The voltage-step method of Vielstich and Delahay⁽⁴⁾ was selected primarily due to the simplicity of instrumentation. This method has been employed previously for the determination of kinetic parameters in molten salts,⁽⁵⁾ although the results obtained in that work have been questioned recently.⁽⁶⁾ Molten fluorides are of great technological importance (Hall process, uses in nuclear technology as in the molten salt reactor⁽⁷⁾ and the fluoride volatility process,⁽⁸⁾ the plating of refractory metals⁽⁹⁾) however, relatively few electrode processes have been studied in these melts (for a partial summary see⁽¹⁰⁾). To our knowledge, the present work is the first attempt to apply a relaxation method to the study of a charge transfer process in molten fluorides.

Experimental

To date the kinetics of the $\text{Ni}^{+2} + 2e \rightleftharpoons \text{Ni}$ process have been studied in molten $\text{LiF-BeF}_2\text{-ZrF}_4$ (65.6-29.4-5.0 mole %) at 497°C. Measurements in LiF-NaF-KF (46.5-11.5-42 mole %) are in progress. The melt is contained in a graphite crucible enclosed in a dry box equipped with a furnace. The experimental arrangement has been described.⁽¹⁾ The working electrode in this work was a nickel rod ($A = 7.5 \times 10^{-3} \text{ cm}^2$) sheathed in hot-pressed boron nitride. The walls of the BN sheath were sufficiently thick ($> 1/8''$), so that no penetration by the melt was observed during the duration of the experiment. The counter electrode was a large nickel spiral. The Ni(II) concentration in the melt was determined by chemical analysis.

The circuit for the voltage step method is essentially that of Laitinen, Tischer and Roe.⁽⁵⁾ Two mercury relays (Clare HG 1002) were used to make sure that the short circuit between the electrodes is broken before applying the voltage step (usually 4 mv.). The oscilloscope (Tektronix 535A) is triggered by the signal obtained across the coil of one of the mercury relays. The signal across the precision measuring resistor (1, 5, or 10 ohms) was fed directly into the plug-in amplifier (Type D or Type CA) of the oscilloscope.

Results and Discussion

The experimental current-time curve (total current, I_T), and other calculated or extrapolated current functions described below, for the Ni(II) concentration of 9.8×10^{-3} moles/liter are shown in Fig. 1. We have followed the procedure used by Laitinen, Tischer and Roe,⁽⁵⁾ except that the charging current, I_{CH} , curve was obtained by the extrapolation of the initial current values according to the equation,

$$I_{CH} = \frac{V}{R_T} \exp\left(-\frac{t}{R_T C_{d.l.}}\right),$$

where R_T is the total resistance in the circuit and $C_{d,1}$ is the differential double layer capacity. This conventional equation for the charging of a capacitor in series with a resistor was used previously⁽⁵⁾ in molten salts. We have found that the initial current values when plotted against time on semilog paper result in a good linear plot; R_T values, calculated from the intercept, are of expected magnitude. Values of $C_{d,1}$, calculated from the slope and the estimated geometrical area of the working electrode, ranged from $186 \mu\text{F}/\text{cm}^2$ to $314 \mu\text{F}/\text{cm}^2$. The double layer capacity increased with time. This is believed to have been caused by adsorption of impurities, diffusing from the boron nitride sheath as well as the melt. It was found that the presence of boron nitride definitely increases the double layer capacity. Additional experiments with unsheathed thin wire nickel electrodes are in progress. The method described above for the calculation of i_{CH} took into account the variation of $C_{d,1}$ with time. Also shown in Fig. 1 is the difference of i_T and i_{CH} , which is the current due to the faradaic process (net faradaic current). The plot of the net faradaic current vs. $t^{1/2}$ is shown in the bottom half of Fig. 1. Similarly to Laitinen et. al., we have extrapolated the linear portion to zero time and then transferred the extrapolation to the top graph. The procedure for the selection of the "effective zero time" was the same as used by Laitinen et. al.⁽⁵⁾ The exchange current density was calculated from the value of current at the "effective zero time" using equation (2) in reference (5). Attempts to apply the corrections suggested by Oldham and Osteryoung,⁽⁶⁾ resulted in continuously increasing values of the exchange current density, although our data obeyed the criteria (equations (17) and (19) reference (6)) proposed by Oldham and Osteryoung⁽⁶⁾ for the presence of kinetic information. It is felt, therefore, that the values of i_0 shown in Table 1, represent the lower limits of i_0 at respective concentrations.

Table I

Exchange Current for Ni/Ni(II) in $\text{LiF}-\text{BeF}_2-\text{ZrF}_4$
(65.6-29.4-5.0 mole %) at 497°C

Concentration of Ni(II), moles/liter	i_0 amp./cm ²
0.982×10^{-2}	7.30×10^{-2}
1.18×10^{-2}	8.32×10^{-2}
1.42×10^{-2}	8.73×10^{-2}
1.75×10^{-2}	11.5×10^{-2}
2.07×10^{-2}	12.8×10^{-2}

From the plot of $\log i_0$ vs. $\log \text{Ni(II)}$ (Fig. 2), the transfer coefficient α was calculated as 0.23 (the slope is $1 - \alpha$). The standard rate constant, k^0 , was found to be approximately 3.2×10^{-3} cm/sec, using the relationship $i_0 = nFk^0 C_{\text{Ni(II)}}^{1-\alpha}$.

References

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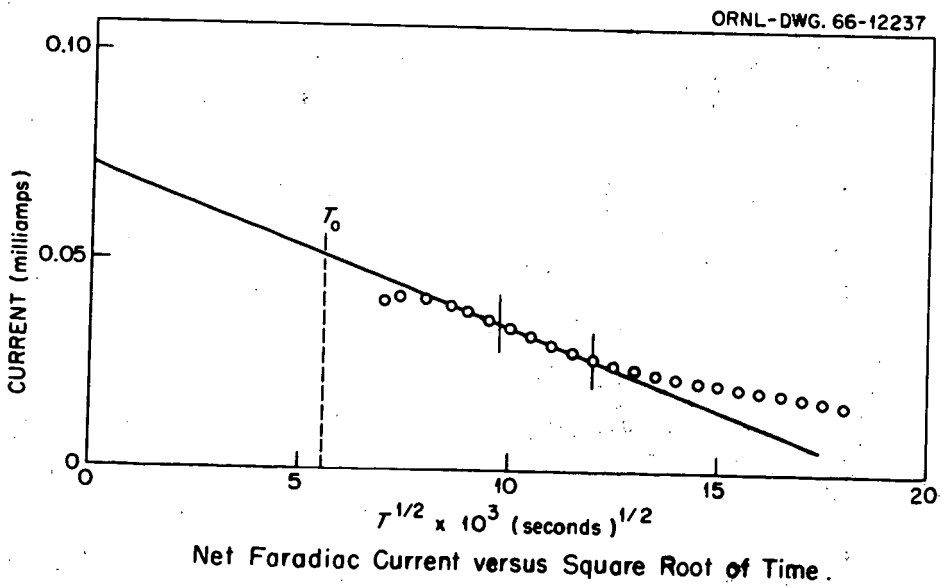
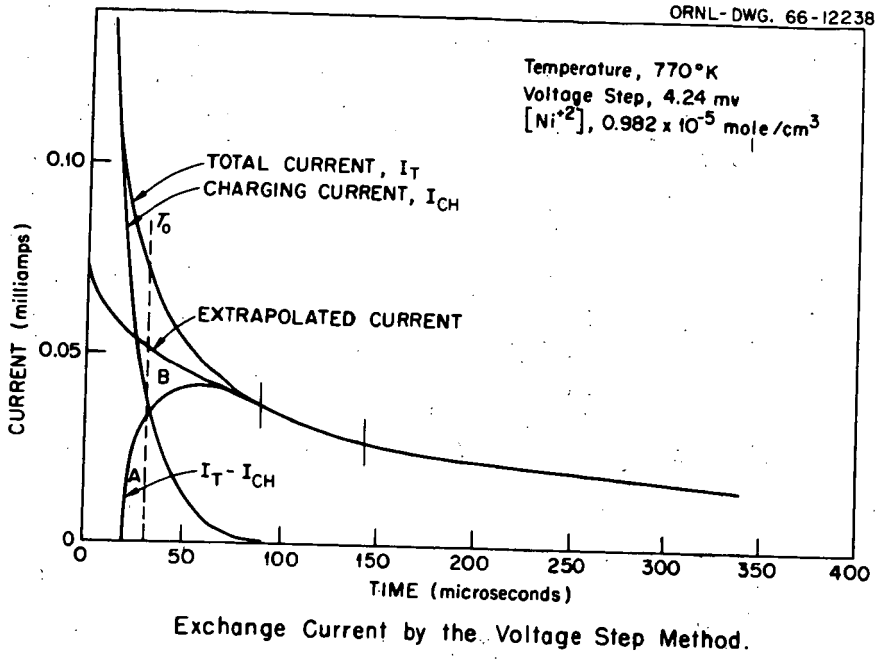
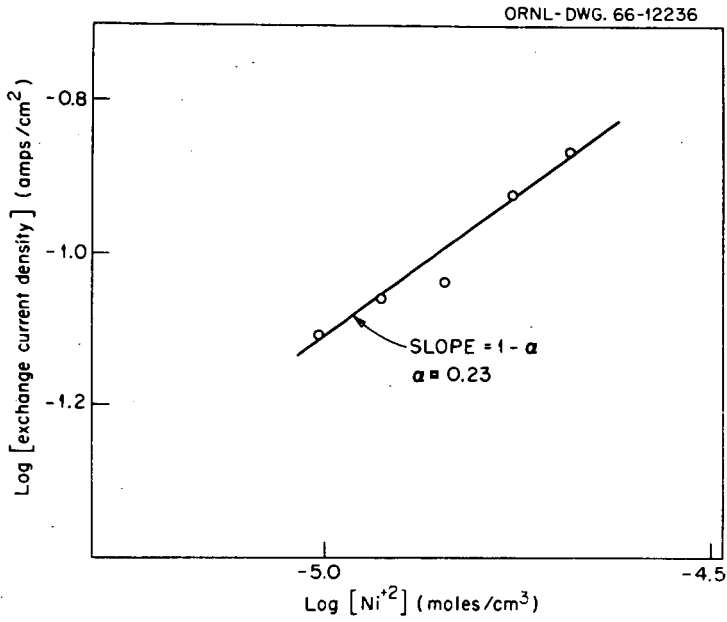


Figure 1



Determination of α for the Ni/Ni²⁺ Couple in Molten LiF-BeF₂-ZrF₄.

Figure 2