GRAPHITE AS MEMBRANE IN A REFERENCE ELECTRODE FOR MOLTEN FLUORIDES BETWEEN 650 AND 800 °C

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ABSTRACT

A reference electrode for use in fluorides melts has been developed and tested. It consists of a nickel wire immersed in a solution of nickel fluoride in LiF-NaF-KF (FLINAK) eutectic. The electrode was contained in a one-end-open graphite cylinder with wall thickness of 1 mm. The exterior was coated with pyrolytic boron nitride (PBN), for electrical insulation, except from cylinder's bottom. The EMF between two electrodes was stabilized within 3 hours after the immersion in the bath and a Nernstian response with temperature was observed. The electrode was found to be stable for more than 30 hours and could be reused with reproducible results. No potential shift was observed in cyclic voltammograms which were obtained, with a lapse of 24 hours, from FLINAK with 0.1 mol % K\textsubscript{2}NbF\textsubscript{7} having as reference the described electrode.

INTRODUCTION

Systematic electrochemical studies of molten fluoride systems, specially in the temperature range of 600 to 850 °C, are difficult to be conducted because of the problems encountered in selecting a reference electrode having all the desired characteristics i.e stability, durability, reversibility, reproducibility and fast response. The commonly used reference electrodes in fluoride melts are:

a) The nickel-nickel fluoride reference electrode contained in a thin-walled boron nitride (BN) envelope. The electrode was developed for potential measurements in molten LiF-NaF-KF [42-11.5-46.5 mole %](FLINAK) at a working temperature of 500 -550 °C (1,2). Boron nitride is slowly impregnated by the melt to provide ionic contact. The wetting occurs in about 6 hours (3) in molten FLINAK. At higher temperatures the BN appears to deteriorate permitting mixing of the melts. Furthermore the boron nitride tube contained a boric oxide binder that dissolved contaminated the electrolyte, and changed the electrode potential.

b) The nickel-nickel fluoride reference electrode system exhibiting a membrane from a single crystal lanthanum trifluoride (4,5). Because of the solubility
of the LaF$_3$ in the fluorides melts a nickel frit with fine porosity was used in order to protect the crystal. The system was tested for temperatures up to 600 °C. On the other hand the single crystal LaF$_3$ is expensive, the assembling of the electrode is more complicated while the crystal cracks after few experiments.

c) The Ni-NiO reference electrode of the third kind with a nickel wire immersed in molten 2LiF-BeF$_2$ with excess NiO and BeO and contained in silica tube (6). The electrode has been tested up to 700 °C.

d) The dynamic Li,K/Li$^+$,K$^+$ reference electrode (7). The thermodynamic explanation for the potential of this reference electrode is unclear while the preparation by a constant current electrolysis before the potential measurement is cumbersome.

From the electrodes described above it is apparent that there is a need for an easy-to-made, durable and having shorter wetting period reference electrode to be used from 700 to 800 °C in fluoride melts. The aim of this work was to develop and quantitatively test such an electrode by using graphite as membrane. The Ni/Ni(II) couple was chosen because its suitability as a reference electrode in molten fluorides has been proven previously (1-5).

EXPERIMENTAL

Chemicals
- LiF; NaF; KF: Merck p.a. grade. The fluoride salts were purified further by melt crystallization. FLINAK was prepared by mixing the recrystallized compounds in a glove-box.
- K$_2$NbF$_7$: Johnson Matthey Electronics.
- Vitreous carbon crucibles: Le Carbone - Lorraine.
- AgF: Aldrich, 99.9+% purity.
- Ni wire: Alfa, 99.99 % purity.
- Ag wire: Alfa, 99.999 % purity.
- Boron Nitride: Carborundum, Combat HP grade.
- NiF$_2$: Cerac, 99.5 % purity.
- Al$_2$O$_3$ tubes: Friedrichsfeld.
- Graphite: Ringsdorff, grade EK-90.

Reference Electrode

The electrode was contained in a one-end-open graphite (grade EK-90, Ringsdorff) cylinder with wall thickness of 1 mm and outside diameter 8 mm. The graphite was isostatic molded and the total open porosity was 14 %. The pore size was 1.5 μm. Permeability for air was 17 x 10$^{-2}$ cm$^2$/sec. The exterior was coated by using CVD with pyrolytic boron nitride (PBN) for electrical insulation. The PBN layer had no porosity. No PBN layer was coated on the surface of electrode’s bottom. The wall thickness in the bottom was 2 mm.

The electrode was isolated from the furnace’s environment with a cover constructed from BN. Electrical insulation for the metal leads of the electrodes was
accomplished by enclosing them in alumina tubes. The alumina tube, the BN cover and the graphite body were held together with the help of BN screws (Fig. 1).

The graphite prior to the filling was immersed in a ultrasonic bath for two hours and then washed with deionized water. In electrode's interior Ni or Ag wire was used in contact with FLINAK and the lead's fluoride salt. Typical resistance of such an electrode is of the order of 2 K ohm over the range 700 - 800 °C.

Instrumentation

A home-made oven with three heating zones and programmable heating controller was used. The furnace was equipped with a Ni tube core and vacuum and/or inert atmosphere could be established in the interior. Al₂O₃ radiation shields were used. Temperature of the bath was measured with an Inconel sheathed Chromel-Alumel thermocouple housed in a closed end alumina tube (Fig. 2).

An EG&G potensiosstat/galvanostat (Model 173) equipped with the model 178 electrometer probe was used for the emf measurements and the application of the desired voltage in the reference electrodes. For the cyclic voltammogram a home-made variable voltage ramp generator was utilised in conjunction with the potensiosstat. The data were recorded in an IBM compatible personal computer an SMM 818 data acquisition card.

RESULTS AND DISCUSSION

The Ni²⁺/Ni° couple in fluoride salts it is known to exhibit a Nernstian behavior (1-5) but is strongly oxidizing when high concentrations of Ni²⁺ are used. Diffusion of dissolved NiF₂ out of the reference electrode could cause oxidation of the materials in the outer half-cell. As an alternative to Ni²⁺/Ni° the Ag⁺/Ag° couple was also tested. The characteristics of the reference electrode were acquired by measuring the deviation of the potential difference between identical designs (stability, reproducibility) or between electrodes having different concentrations of NiF₂ or AgF (Nernstian response). Reversibility was tested by superimposing a potential difference on the EMF of two identical electrodes. The reliability was verified by observing the potential difference with time of the reduction and oxidation waves of cyclic voltammograms of K₂NbF₇ in a cell having the proposed reference electrode.

Stability and Reproducibility

Reference electrodes having either Ni/NiF₂ (1 mol % in FLINAK) or Ag/AgF (1 mol % in FLINAK) were immersed in the alkali fluoride eutectic at 700 °C. The EMF was stabilized in a period of 3 hours after their immersion in the molten bath. The wetting period was almost half of what has been reported elsewhere (3). EMF remained virtually unchanged (± 2 mV) for more than 30 hours. The same electrodes were cleaned, refilled and re-immersed again in the FLINAK eutectic. The wetting period was again approximately 3 hours (Fig. 3). As can be seen in Fig. 3 no significant difference in behavior was observed between electrodes having

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either the Ni/Ni(II) or the Ag/Ag(I) couple.

Nernstian Response

The EMF values between two electrodes having different molar fraction of NiF₂, $x_1=0.002$ and $x_2=0.001$ were recorded at different temperatures. The experimental as well as the theoretical emf values expected from Nernst equation for the cell:

$$\text{Ni/Ni}^{2+}(x_1=0.002)/\text{Graphite}/\text{FLINAK}/\text{Graphite}/\text{Ni}^{2+}(x_2=0.001)/\text{Ni}$$

are presented in Table I.

Table I: EMF Values Between Two Reference Electrodes with $[\text{Ni}^{2+}]_1/[\text{Ni}^{2+}]_2=2$

| Temperature °C | Theoretical\(^\d\) (mV) | Experimental (mV) |
|---------------|--------------------------|-------------------|
| 680           | 27.4                     | 27.6              |
| 710           | 28.3                     | 28.9              |
| 730           | 28.9                     | 29.3              |
| 790           | 30.6                     | 31.1              |

(1). Assuming that the activity coefficient of Ni\(^{2+}\) in both electrodes are equal to 1.

The experimental values of Table I indicate that the electrodes exhibit a Nernstian behavior since the difference from the theoretical values are negligible and therefore the junction potential is insignificant.

Reversibility

On the EMF of two identical electrodes filled 1 mol % AgF, a ± 1 V and ± 0.5 V were superimposed for 60 and 30 s respectively. The response with time is represented in Fig. 4. The potential difference decays to a stable value within 5 minutes.

Potential Shift

Cyclic voltammograms of 0.1 mol % K₂NbF₇ in FLINAK at 700 °C were obtained over a period of 24 hours. A Pt working electrode (0.5 mm diameter), a Ni/NiF₂ (0.1 mol %)/graphite membrane reference electrode and the glassy carbon crucible as the counter electrode (exposed area 30 cm²) were used. A Pt lead was utilised to establish the current flow to the crucible. No shift of the reduction-oxidation waves against the reference electrode was observed with time (Fig. 5). The explanation for the reduction and oxidation waves of NbF₇\(^{2-}\) has been reported elsewhere (8-9).
CONCLUSIONS

A rather inexpensive and easy to made Ni/Ni(II) reference electrode contained in an one-end-open PBN covered graphite cylinder, except from the electrode's bottom has been constructed. No PBN layer was coated on cylinder's surface bottom. Electrode's potential stabilizes within 3 hours while EMF remains stable for more than 30 hours. The electrode can be reused with no loss of its stability and exhibits a Nernstian response with temperature up to 800 °C. The EMF after an application of ±1 V perturbation decays to a stable value within 5 minutes. The reference electrode was used in cyclic voltammograms of 0.1 mol % K₂NbF₇ in FLINAK. No potential shift was observed in the reduction and oxidation waves indicating the stability of the electrode.

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Figure 1. Reference Electrode.

Figure 2. Furnace’s schematic during an EMF measurement.
Figure 3. A: EMF vs. time between two electrodes with Ni/NiF₂ (1 mol % in FLINAK); B: EMF vs. time between two electrodes with Ag/AgF (1 mol % in FLINAK).

Figure 4. EMF vs. time between two electrodes with Ag/AgF (1 mol % in FLINAK). A ± 1 V and ± 0.5 V were superimposed for 60 and 30 s respectively on the EMF.
Figures 5. Voltammograms of 0.1 mol % K₂NbF₇ in FLINAK at 700°C obtained with a Pt working electrode (0.5 mm diameter), Ni/NiF₂ (0.1 mol %)/graphite membrane reference electrode and glassy carbon counter electrode. Scan rate 0.4 V s⁻¹ Scan ± 1250 mV Voltammograms A and B were recorded 12 and 24 hours respectively after the immersion of the electrodes in the melt.