



Dynamic Reference Electrode development for redox potential measurements in fluoride molten salt at high temperature



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ABSTRACT

Measurement of redox potential in fluoride media is a major problem due to the difficulty to design a reference electrode with high stability, high mechanical resistance and high accuracy. In the frame of molten salt reactor studies, a dynamic reference electrode (DRE) is developed to measure redox potential in fluoride molten salt at high temperature. DRE is based on the *in-situ* generation of a transient redox system. The choice of the redox couple corresponds to the cathodic limit of the molten salt considered. As a preliminary step, the demonstration of feasibility of generating a DRE was done in LiF-NaF-KF (46.5–11.5–42 mol%) media at 500 °C. In this salt, the reference redox system generated by coulometry at applied current is KF/K, metallic potassium being electrodeposited on a tungsten wire electrode. The validation of the DRE response and the experimental optimization parameters for DRE generation were realized by following the NiF₂/Ni redox potential evolution as a function of NiF₂ concentration in the fused salt.

The current value applied for DRE generation was optimized. It depends on the amount of metallic cations contained in the fused salt and which can be electrochemically reduced simultaneously during the DRE generation. The current corresponding to the DRE generation has to be 4 times greater than the current corresponding to the reduction of the other elements.

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1. Introduction

The molten salt fast reactor (MSFR) is an innovating concept of the molten salt reactor (MSR) developed by CNRS (France) since 2004 [1–4]. This reactor is a nuclear concept of Generation IV, currently in a developing phase (particularly in the frame of the European project SAMOFAR supported by HORIZON H2020), and derived from other concept described in the reference [5]. This concept is designed for the use of a liquid nuclear fuel composed of a mixture of fluoride salts (liquid in the reactor operation temperature range, 650–850 °C), which circulates from the reactor core to the heat exchangers. This reactor is adapted to work under thorium fuel cycle (Th²³²-U²³³). The nuclear fuel retained for the MSFR is constituted of the fluoride salts, LiF-ThF₄-(UF₄-UF₃) (77–19–4 mol%). In this concept, the structural materials corrosion is an issue, because of the use of a liquid nuclear fuel composed of materials and fuel salt. Several factors promote the corrosion of these materials, such as oxidizing impurities (O₂, H₂O, F₂), secondary products of chemical reactions (HF) or fission products,

as well as the high working temperature. Also, an alteration of the chemical and physical properties of the salt has been reported due to the temperature gradient between hot and cold points in the circulator which causes a variation of the salt chemical composition [6–8]. Currently, the development and evaluation of new materials (essentially Ni-based alloys with low Cr amounts) that are more resistant to operating conditions of the reactor constitutes a large research focus. On the other hand, the development of methods to prevent corrosion is an approach of major interest to avoid the chemical damages. It was demonstrated that the redox potential of the salt is the most influential parameter in the structural materials corrosion process. Therefore the fuel redox potential control can be used for materials oxidation prevention. The redox potential can be controlled using an internal redox “buffer” which fixes the molten salt potential. The redox buffer chosen for MSFR application is constituted of the two soluble oxidation states of uranium, UF₄ and UF₃. In this way, the fuel salt redox potential is given by the Nernst relation:

$$E_{\text{UF}_4/\text{UF}_3} = E_{\text{UF}_4/\text{UF}_3}^{\circ} + \frac{2.3RT}{nF} * \log \frac{[\text{UF}_4]}{[\text{UF}_3]} \quad (1)$$

Where, E is the redox potential of the salt, E° is the apparent standard potential of UF₄/UF₃ (V), R is the ideal gas constant

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($=8.314\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), T is the temperature (K), n is the number of exchanged electrons, F is the Faraday's constant ($=96500\text{C}$), $[UF_4]$ and $[UF_3]$ are respectively the concentrations of UF_4 and UF_3 in the fuel salt.

The relation (1) shows that a modification of the $[UF_4]/[UF_3]$ ratio will cause a redox potential variation of the fuel salt. An increase of the salt potential leads to the oxidation of structural materials, particularly oxidation of Cr [6]. The redox potential has to be measured *in-situ* in the reactor core because it was shown that the potential of the fuel salt increases with the operation time because of the fission reaction [6]. The control (and decrease) of the potential can be realized by the addition of given amounts of reductive element, metallic uranium for instance. Then, the chemical reaction (2) will occur in the salt:



Gibilaro et al. [9] have shown by electrochemical techniques a fast kinetic of this reaction in an inactive fluoride salt.

The measurement of the redox potential in the fuel salt requires a reference electrode with high mechanical resistance and high accuracy. The concentration ratio $[UF_4]/[UF_3]$ can vary from 10 to 100 which corresponds to a potential range of 0.2 V. A corrosion study has been realized by the Oak Ridge National Laboratory [10]: metallic samples were introduced in molten salts which composition varies from 10 to 100. At the end of the corrosion tests, the samples were characterized by SEM analysis. It was observed that for a ratio lower than 60, no corrosion is observed. This was observed by SEM characterization of alloys dipped in several compositions of molten salts. The aim of this paper is to present a methodology to prepare an *in-situ* dynamic reference electrode by applying a cathodic current in a molten salt containing metallic cations and to optimize the internal generation conditions. As a preliminary step, tests were done in the inactive fluoride salt LiF-NaF-KF-NiF₂ (0.1–1 mol%) molten salt at 500 °C.

2. State of the art

Various reference electrodes have been developed for their use in molten fluorides [11]. The most serious problems encountered in the development of reference electrodes for fluorides deal with containment and materials of construction. Alumina rod that was wet by the solvent was employed as the salt bridge, but some solubility of alumina in the solvent and the presence of undesired oxide ions were observed [12,13]. Boron nitride (BN), which is normally an insulator in fluoride melt, has been used. It is slowly impregnated by the melt to provide ionic contact [14–16]. In these conditions a compartment of BN is filled with the molten salt containing generally NiF₂ and a Ni wire ensuring the electrical contact. The wetting of BN occurs in about 24 hr in molten LiF-NaF-KF while a longer period is usually required for more acidic media (10–14 days in LiF-BeF₂-ZrF₄ molten salt at 500–550 °C [14]). BN coated graphite was also tested as reference electrode [17]. A reference electrode for molten fluorides employing a single-crystal LaF₃ membrane for separation was also described and used for electrochemical determinations [18–20]. Generally the redox system considered for the reference electrode is Ni(II)/Ni because it is a reversible system in fluoride solvents [14]. However, prolonged contact with fluoride melts will eventually deteriorate the BN because of a chemical reaction between NiF₂ and BN [11]. The redox system AgCl/Ag has also been employed in the BN container [16] but this redox system cannot be used at temperatures higher than 960 °C due to silver fusion. In this case, the molten salt introduced in the BN container is a chloride media, AgCl/Ag being a reversible system in these conditions. Pizzini [21] used a BN compartment containing a platinized

platinum foil. A stable potential is observed after 10 mn of hydrogen bubbling.

Another type of references is based on the generation of an internal reference electrode. This option was retained for the MSFR application. Indeed, the reference electrode being immersed in the reactor core, it requires a high mechanical resistance which is not reached by the use of BN containment. The reference electrode has to be made of a metallic rod, chemically inert, stable at high temperatures, sensitive to the change of medium composition, with a high corrosion resistance and high mechanical resistance. Moreover, the reference redox system has to be reversible. Previous works present the *in-situ* electrochemical generation of a reversible redox system by an anodic [22] or cathodic reaction [23–25]. Ema et al. [23] have developed a dynamic reference electrode of Li, K/Li⁺, K⁺ for the electrochemistry in LiF-KF eutectic melt. This electrode is obtained by a constant current applied on a nickel rod. A Li-K alloy is deposited in a molar fraction of 2:1. The equilibrium potential of the alloy immersed in the fluoride salt is in agreement with thermodynamical calculations and measurements of HF/H₂ gas electrode. Stability and reproducibility have been obtained for the measurements. Adhoum et al. [22] have studied the Na⁺/Na, Ni²⁺/Ni, Mo³⁺/Mo and the Fe²⁺/Fe redox systems for a future use as dynamic reference electrode in the molten sodium fluoride at 1025 °C. The electrochemical study through convolution voltammetry shows the reversibility of Fe²⁺/Fe system. The small dispersion of the measurements allows this system to be used as a dynamic reference electrode. More recently, Afonichkin et al. [24], have developed a device for redox potential measurements (DRPM) in LiF-NaF-BeF₂ (15–58–27) mol% molten salt at 600 °C. The DRPM is based on a system with three electrodes and two of them are used for the dynamic reference electrode generation. The dynamic reference electrode is made of a tungsten electrode covered by metallic Be, the reference redox system being Be(II)/Be. An accuracy of $\pm 5\text{mV}$ is obtained for this dynamic reference electrode. The performance of DRPM has been tested in a loop under thermal convection during 1200 h. The on-line tests showed the stability and reliability of the device. Qiao et al. [25] have developed an internal reference electrode by electrochemical formation of Au₂Na alloy in FLiNaK molten salt.

3. Technical

LiF, NaF, KF, NiF₂ are provided by Sigma Aldrich (>99% purity) W, Ni are provided by Goodfellow (>99.9% purity). Graphite is provided by Carbon Lorraine (>98% purity).

The molten salt is a mixture of LiF-NaF-KF (46.5–11.5–42) mol% known as FLiNaK. The FLiNaK mixture is introduced and mixed in a glassy carbon crucible (HTW Hochtemperatur-Werkstoffe GmbH) disposed in a cell. The cell is made of Pyrex and constituted of two parts (top and bottom). The air tightness is maintained using a locking screw. The electrochemical cell is then introduced in a tubular furnace (80 cm diameter) connected to a regulation monitor provided by THERMOLAB/Spain. Electrochemical measurements are performed with a potentiostat-galvanostat model PAR 263A coupled with a PC computer.

The purification of the salt is performed by keeping the cell under vacuum for 24 h at 573 K. next, the mixture is melted by increasing the temperature to 773 K. All the experiments are performed under argon gas (Air Liquide) flow at 773 K. NiF₂ is added in the molten salt at various concentrations ranging between 0.1 and 1 mol%.

The working electrodes are prepared using a Ni wire (1 mm diameter) and a W wire (1 mm diameter). The auxiliary electrode used for DRE generation is a graphite rod (3 mm diameter, Carbon

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