Transactions of the Korean Nuclear Society Autumn Meeting
Gyeongju, Korea, October 29-30, 2026

Electrochemical Behavior of OH^- in Molten Chloride Salts

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Keywords : molten chloride salt, moisture detection, electrochemical monitoring, hydroxide ion, barium hydroxychloride

1. Introduction

Molten salt reactors (MSRs) are being considered as an alternative to conventional oil-based propulsion systems to meet increasingly stringent CO_2 emission regulations in the maritime sector [1,2]. NaCl-UCl_3, KCl-UCl_3 and NaCl-KCl-UCl_3 salt systems have been considered promising fuel salt candidates for MSRs because of their favorable thermophysical properties, high solubility of fissile species, resistance to radiation damage, low vapor pressure, and relatively low corrosivity [3]. For long-term operation, reactions with oxygen or moisture can alter the molten fuel salt composition, requiring continuous monitoring. The behavior of oxygen in molten fuel salts is relatively well understood: oxygen can generate oxide ions and uranium oxides, shifting the redox state of the fuel salt toward more oxidizing conditions. In contrast, the behavior of moisture is more complex because it consists of two elements, H and O. As a fundamental study to better understand the behavior of moisture, this study investigated the behavior of OH^- in NaCl-KCl and NaCl-KCl-$BaCl_2$ molten salts. Barium was selected as a representative fission product. Moisture was assumed to react with chloride ions to form OH^- according to the following reaction (**Equation 1**):

$$H_2O + Cl^- \rightarrow HCl + OH^- \quad (1)$$

2. Methods

2.1 Chemical Preparation

The initial compositions of the salts are summarized in **Table 1**. Anhydrous NaCl (sigma-aldrich, 99.99%) and KCl (sigma-aldrich, 99.95%) were used as the base salts. Prior to salt preparation, NaOH (Sigma-Aldrich, 98%) and anhydrous $BaCl_2$ (Sigma-Aldrich, 99.9%) were preheated at 300 °C to remove residual moisture. The NaCl-KCl-NaOH salt was prepared by mixing NaCl and KCl at a molar ratio of 50:50. The mixture was heated to 700 °C, followed by the addition of 0.34 wt% NaOH. The NaCl-KCl-$BaCl_2$ salt was prepared by mixing NaCl, KCl, and $BaCl_2$ at a molar ratio of 49.8:49.8:0.4. The NaCl-KCl-$BaCl_2$-NaOH salt was prepared by heating the NaCl-KCl-$BaCl_2$ salt to 700 °C, followed by the addition of 0.49 wt% NaOH. A NaCl-KCl-BaOHCl salt was prepared by mixing NaCl and KCl at a molar ratio of 50:50, heating the mixture to 700 °C, and subsequently adding 0.48 wt% synthesized BaOHCl powder. The synthesis procedure for BaOHCl is described below.

Table 1. Initial salt compositions.

Salt	Composition (mol%)
NaCl-KCl-NaOH	49.7-49.7-0.6
NaCl-KCl-$BaCl_2$	49.8-49.8-0.4
NaCl-KCl-$BaCl_2$-NaOH	49.4-49.4-0.3-0.8
NaCl-KCl-BaOHCl	49.9-49.9-0.2

BaOHCl was synthesized from $BaCl_2$ and $Ba(OH)_2$ (Sigma-Aldrich, 95%). The two reagents were mixed at an equimolar ratio and pressed into pellets at room temperature using a pelletizer. The resulting pellets were heated to 450 °C and maintained at this temperature for 8 hours to synthesize BaOHCl according to **Equation 2**. The synthesized BaOHCl powder was then characterized by X-ray diffraction (XRD) to confirm its phase composition (**Figure 1**).

$$BaCl_2 + Ba(OH)_2 \rightarrow 2BaOHCl \quad (2)$$

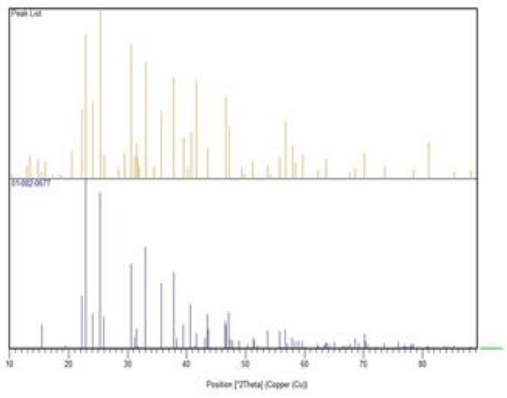


Figure 1. Comparison of the XRD patterns of the synthesized BaOHCl powder and the reference BaOHCl pattern (PDF No. 01-082-0677).

2.2 Electrochemical Analysis

The electrochemical analysis was conducted using a three-electrode cell. A tungsten wire with a diameter of

1 mm was used as the working electrode. The reference electrode consisted of a silver wire immersed in NaCl-KCl containing 1 wt% AgCl and encapsulated in a mullite tube. A tungsten wire with a diameter of 2 mm was used as the counter electrode. Electrochemical measurements were performed using a potentiostat (PARSTAT 2000A).

3. Results and Discussion

For application to MSR systems, the potential range available for electrochemical monitoring should be determined considering the redox reactions of uranium in the fuel salt. The potentials of these reactions depend on both uranium concentration and temperature. At relatively high uranium concentrations at 550 ℃, the U^{3+}/U^{0} and U^{4+}/U^{3+} redox reactions have been reported to occur at approximately -2.5 V and -1.5 V (vs. Cl^{-}/Cl_2), respectively [4]. At lower uranium concentrations at 700 ℃, the corresponding potentials were reported to be approximately -2.4 V and -1.2 V (vs. Cl^{-}/Cl_2), respectively [5]. Although the corresponding redox potentials at high uranium concentrations at 700 ℃ have not yet been clearly established, these reported values suggest that the potential range from approximately -1.0 to 0.0 V (vs. Ag/Ag^{+}) could be considered a practical range for electrochemical monitoring.

Figure 2 compares the cyclic voltammetry (CV) curves recorded before and after the addition of NaOH. Both CV measurements were conducted using the following potential sweep sequence: from 0 V (vs. open-circuit-potential, OCP) to -1.4 V, then to +1.3 V, and finally back to 0 V (vs. Ag/Ag^{+}). Following the addition of NaOH, several new redox peaks appeared in the CV curve. Among these peaks, the anodic peak at around -0.1 V falls within the proposed monitoring range and therefore selected as a candidate electrochemical signal for detecting moisture intrusion.

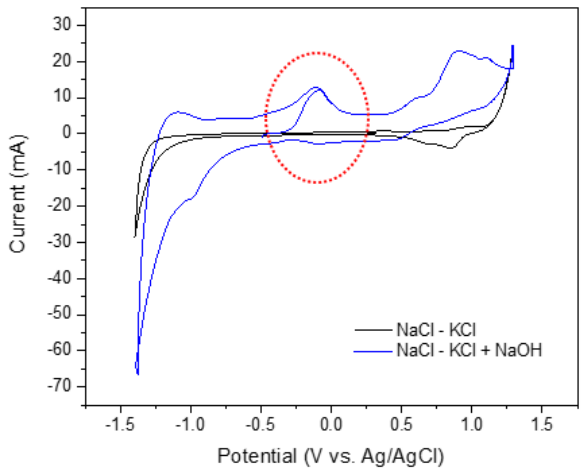


Figure 2. Comparison of CV curves for NaCl-KCl before (black) and after (blue) the addition of NaOH.

Figure 3 shows the linear sweep voltammetry (LSV) curves of NaCl-KCl-NaOH recorded over time. The oxidation peak at approximately -0.1 V gradually decreased with time, indicating that OH^{-} is unstable under molten salt conditions. Because the experiment was conducted in an open system, volatile species could escape from the system. Therefore, it was proposed that OH^{-} was converted to O^{2-} through a reaction involving the evolution of H_2O (g) (**Equation 3**).

$$2OH^{-} \rightarrow O^{2-} + H_2O \quad (3)$$

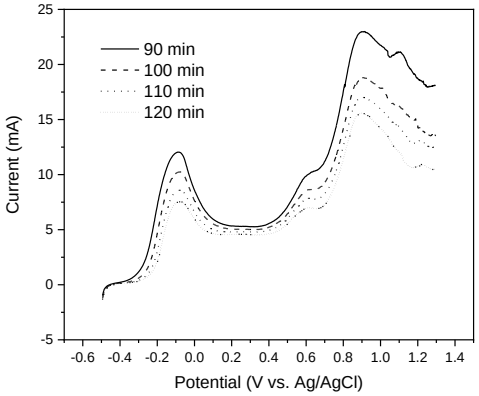


Figure 3. LSVs of NaCl-KCl-NaOH recorded over time

Figure 4 compares the CV curves of NaCl-KCl-$BaCl_2$ recorded before and after the addition of NaOH. The CV curve after NaOH addition was recorded one day after the addition. A new reduction peak appeared at approximately -0.75 V (vs. Ag/Ag^{+}), suggesting that $BaCl_2$ reacted with OH^{-} to form a new Ba-containing species.

It is known that $MgCl_2$ forms MgOHCl through reaction with OH^{-} ions [6]. Given that both Ba and Mg are alkaline-earth metals, $BaCl_2$ was expected to exhibit similar chemical behavior. Therefore, BaOHCl was considered a possible reaction product under molten-salt conditions.

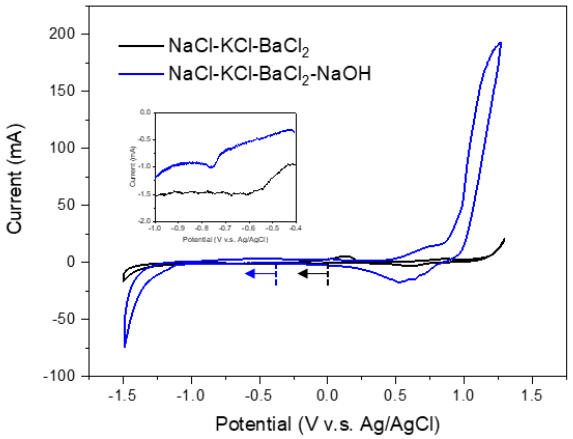


Figure 4. Comparison of CV curves for NaCl-KCl-$BaCl_2$ (black) and one-day after the addition of NaOH (blue).

Figure 5 compares the LSV curves of NaCl-KCl with and without BaOHCl. BaOHCl was prepared according

to the procedure described in the Methods section. A reduction peak was observed at approximately -0.75 V (Ag/Ag^+), which is consistent with the reduction peak observed in **Figure 4**. This agreement supports the hypothesis that the reduction peak appearing after the addition of NaOH to NaCl-KCl-$BaCl_2$ is associated with the formation of BaOHCl (**Equation 4**).

$$BaCl_2 + OH^- \rightarrow BaOHCl + Cl^- \quad (4)$$

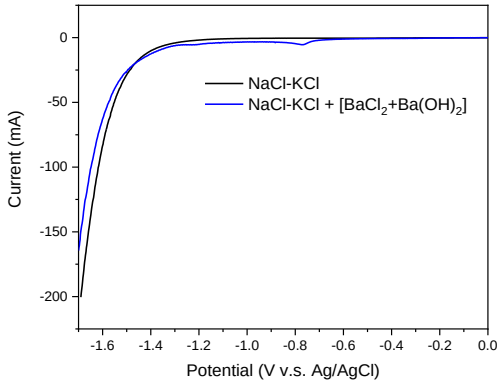


Figure 5. Comparison of CV curves for NaCl-KCl before (black) and after (blue) the addition of BaOHCl.

4. Conclusions

This study investigated the behavior of OH^- in molten salts as a fundamental study for monitoring moisture intrusion in chloride-based molten fuel salts. When OH^- was introduced into molten alkali chloride salts at high temperatures, an oxidation peak appeared at approximately -0.1 V (vs. Ag/Ag^+) and continuously decreased with time, indicating that OH^- was unstable under molten salt conditions. It was suggested that OH^- gradually converted to O^{2-}, likely accompanied by the evolution of H_2O (g). Additionally, in the presence of species capable of reacting with OH^-, hydroxide-containing compounds could be formed. In the $BaCl_2$-containing system, the formation of BaOHCl was suggested by the appearance of a reduction peak at approximately -0.75 V (vs. Ag/Ag^+).

Acknowledgements

This work was supported by the Nuclear Safety Research Program through the Korea Foundation Of Nuclear Safety (KoFONS) using the financial resource granted by the Nuclear Safety and Security Commission (NSSC) of the Republic of Korea. (RS-2025-02303657) and by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Climate, Energy & Environment (MCEE) of the Republic of Korea (No. 20224000000120).

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