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Electrochemical Approaches for Assessing Concentrations and Properties in a Molten Salt Thermal Convection Loop(MSTCL)

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1. Introduction

Molten salt reactors are one of the generation IV reactors in which a molten salt mixture is used as a coolant and as a nuclear fuel itself. It is actively studied because it has the advantages of high thermal efficiency, economy, and safety [1]. Among the various molten salts, chloride-based salts are suitable as fast spectrum reactors [2]. However, due to the corrosive properties of high-temperature molten salts, compatibility of chloride-based salts with structural materials is a major consideration [3]. Iron-based or nickel-based alloys considered as structural materials are composed of alloying elements such as Fe, Ni, Cr, Mn, Mo, etc. When these elements are dissolved in the molten salt by corrosion reactions, they exist as ions under redox conditions. The electrochemical method can thus be used to conduct real-time concentration monitoring of the alloying element in situ.

In this study, electrodes were designed for long-term concentration monitoring. The electrochemical behavior was investigated in a natural convection loop in which a $NaCl$-$MgCl_2$ eutectic salt circulates. To investigate the electrochemical behavior, open circuit potential and cyclic voltammetry methods were applied.

2. Methods

In a study previously conducted, ICP-MS analysis results were compared before and after operating the loop. The result showed the concentration of elements that can dissolve from base metals such as iron and chromium increased [4]. Therefore, electrodes were fabricated to monitor the concentration of corrosion products generated during the long-term operation of the loop and electrochemical measurements were performed.

Fig 1 is an actual picture and schematic of the Molten Salt Thermal Convection Loop used in the experiment and indicates the location where the temperature is measured. Electrochemical measurements were conducted at the all point where temperature was measured. The electrochemical measurement equipment was a Solartron 1470E from Ametec Inc. The electrochemical measurements were performed in two parts, utilizing simultaneous multi-channel measurement, as the instrument could collect data from eight points at a time.

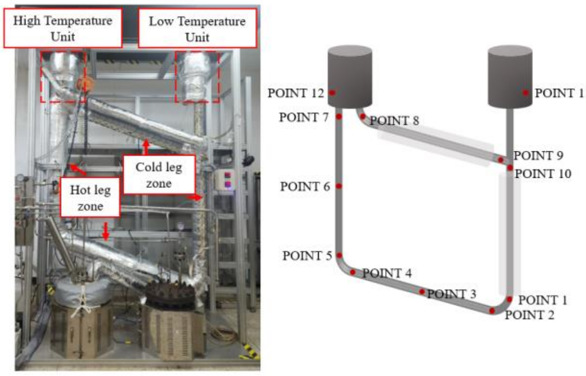

Fig 1. Design of thermal convection loop and the location of the electrodes

2.1 Electrodes

Tungsten wires served as the working electrode and the quasi-reversible reference and counter electrodes. All electrodes were kept independent using alumina ceramic with four holes. Tungsten electrodes were considered for use as quasi-reference electrodes due to their high stability and longevity in salt systems [5]. Fig 2 shows the configuration of the electrodes fitting into the loop. For points 1 to point 10 all used tungsten wire with a diameter of 0.5 mm. The electrode area was fixed using compression seal feedthrough fitting (TG-20-A4-T, Conax) with a 7 mm extrusion from the alumina tube. Electrodes of point 11 and point 11 were used tungsten rods with a diameter of 1 mm, and the length of the working electrode were fixed at 10 mm and 20 mm.

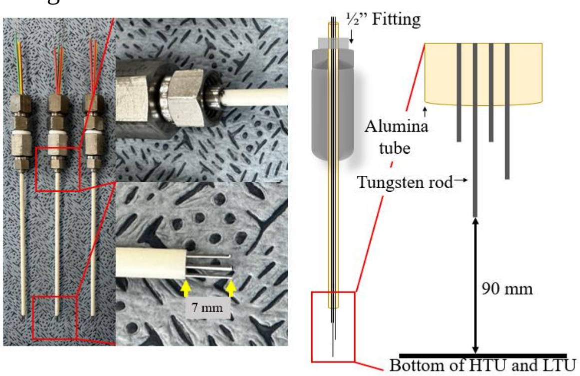

Fig 2. Electrodes for Loop (Left: Electrode for Hot Leg and Cold Leg, Right: Electrode for HTU and LTU)

3. Result

The open-circuit potentiometry(OCP) was measured for 300 seconds and then the cyclic voltammetry(CV) was measured at a scan rate of 0.8 V/sec.

Fig. 3 shows data for OCP measured on the same day at all locations, obtained through simultaneous multi-channel measurement. The temperature at each point was compared to the potential change over time. OCP measures the equilibrium potential at the electrode surface and have difficulty to measure when multiple active species are present in the salt [6, 7]. In this study, we found that the OCP was measuring close to zero cross all positions. However, at higher temperatures of over 800 K, the data from the OCP measurements showed a value that is more unstable than 800 K or less.

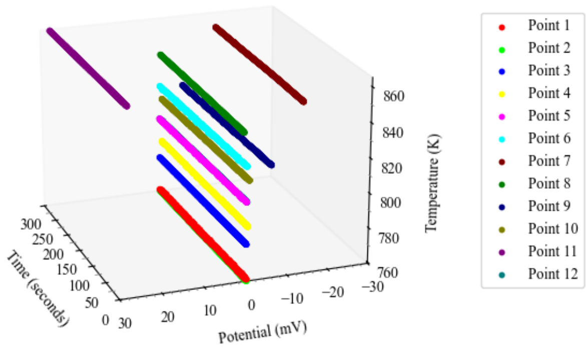

Fig 3. Open circuit potentiometry datas on W electrode at each position

Fig. 4 shows cyclic voltammograms measured on the same day at point 2, point 7, point 8, point 9. Four points were set to show the CV result according to the temperature increase. The reduction peak occurs around -0.1 V at all four temperatures, although there is a temperature-dependent shift, and a reduction peak around 0.3 V is observed for the relatively low temperature data, 759 K. As the temperature increases, the peak tends to shift toward the negative side.

Table 1 shows the peak current values at each location. As the temperature changes, the value of the cathodic peak current does not change significantly, around -0.03 A. However, for anodic peak currents, the temperature increases as the anodic peak currents increase.

Table I: Peak Currents in Cyclic Voltammograms

Position	Temp(K)	I_{pc} (A)	I_{pa} (A)
Point 2	759	-0.0290	0.0978
Point 7	856	-0.0303	0.1877
Point 8	843	-0.0299	0.1759
Point 9	823	-0.0331	0.1558

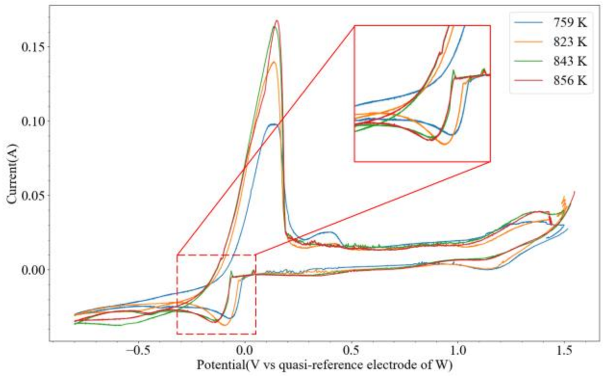

Fig 4. Cyclic voltammograms on W electrode by temperature As the temperature increases, the peak tends to shift toward the negative side.

4. Conclusions

The electrochemical experimental methods cyclic voltammetry and open circuit potentiometry were used to measure NaCl-$MgCl_2$ eutectic salt circulating within a molten salt thermal convection loop. W electrode was used as working electrode, quasi-reference electrode, and counter electrode. The behavior of the OCP data and the shifts in the current peak with temperature were observed. In this way, electrochemical data of the salt cycling in real time can be obtained. In future work, The electrochemical behavior will be investigated through the analysis of electrochemical data on alloy elements at various concentrations and temperatures. These data will allow us to analyze the ionic species and their concentrations in the data measured in the loop. The change in concentration could be cross-checked through ICP analysis of the salt circulating the loop.

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