A Quartz Tube Based Ag/Ag^+ Reference Electrode with a Tungsten Tip Junction for an Electrochemical Study in Molten Salts

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A newly designed Ag/Ag^+ reference electrode in a quartz tube with a tungsten tip junction (W-tip-Quartz- REF) was fabricated and its electrochemical performance was compared with a conventional Pyrex tube-based Ag/Ag^+ reference electrode (Py-REF). The results of the electrochemical potential measurements with the W-tip-Quartz-REF and the Py-REF in the LiCl-KCl eutectic melts for a wide temperature range proved that the oxide layer on the surface of the tungsten metal tip provided a high ionic conduction. Stability of our newly designed W-tip-Quartz-REF was tested by measuring a junction potential for 12 hours at 700°C. The results of the cyclic voltammetric measurement indicated that the Ag/Ag^+ reference electrode in the quartz tube with a tungsten tip junction can provide a good performance for a wide temperature range.

Key Words: Reference electrode, Quartz tube, Electrochemical, Eutectic melts

Introduction

Pyrochemical processing of nuclear fuels using a molten salt as a solvent is regarded as one of the promising options for a future spent nuclear fuel management.[1] Molten salts are known as suitable media for electrorefining and electrowinning of metal. In order to reach a better understanding and control of these metal deposition processes, accurate knowledge of the electrochemical deposition mechanism is essential. Therefore, many electrochemical studies of actinides and lanthanides in various molten salts have been carried out in the past decade.[2,3] However, electrochemical studies of a molten salts system, specially in the temperature range of 450 to 90 0℃, can incur many difficulties due to the problems encountered in selecting a reference electrode with all the desired characteristics i.e stability, durability, reproducibility and also fast response.

In electrochemical studies, a three-electrode cell incorporating a stable reference electrode is essential to avoid an uncertainty of the electrode reactions. An Ag/Ag^+ electrode is a conventional reference electrode used for a molten salts media such as LiCl and LiCl/KCl eutectics. Pyrex, so called sodium glass, is commonly used as a reference electrode at a molten salts temperature between 450 and 600°C, since it can be fabricated easily into a thin-wall tube and thus provide a sufficient ionic conductivity.[4-6] It cannot be used at the temperatures above 600°C, since it can be deformed easily due to its low melting point (820°C).

Quartz is commonly used in various research fields especially at a high temperature up to 1200°C, since it becomes soft at a temperature around 1400°C. Considering that a silver wire in an electrode has a melting point at around 962℃, a quartz tube-based electrode with the combination of a quartz tube and a silver wire could only be used for a working temperature up to ~ 950°C. P. Gao *et al.*[7] tested a quartz sealed Ag/AgCl reference electrode for a $CaCl_2$ molten salt system. This reference electrode revealed a successful performance from an electrochemical analysis in $CaCl_2$ based molten salts in the temperature range between 700 and 950°C. This quartz based electrode, however, had a major drawback due to its high electric resistance at a temperature below 700°C. For example, the resistance of the quartz electrode measured at 600°C was 4×10^5 ohm.

In this study, an Ag/Ag^+ reference electrode in a quartz tube was fabricated with a tungsten tip junction which contains a porous metal oxide layer for an ionic conduction, and then its performance for an electrochemical measurement was assessed in high temperature molten salts between 450 and 600°C.

Experimental and Methods

Chemicals and instrumentation. Lithium chloride (LiCl)/ potassium chloride (KCl) eutectic salts (anhydrous beads) were obtained from Aldrich Co. Ltd. (purity ≥ 99.999%). Sliver chloride (AgCl) was purchased from Alfa Aesar (purity ≥ 99.998%). All the chemicals were used without further purification.

The electrochemical setup used for the voltammetric studies is shown in Fig. 1. The electrochemical reaction vessel

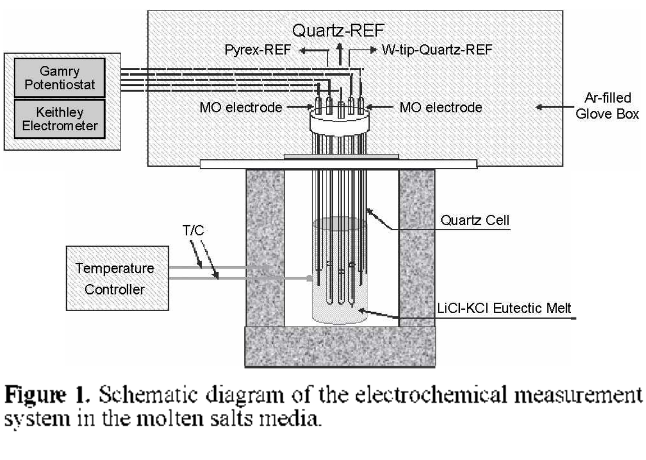

Figure 1. Schematic diagram of the electrochemical measurement system in the molten salts media.

was made of a quartz tube (350 mm in length, 40 mm outer diameter and 2 mm in wall thickness) by using a glass blowing technique. Two molybdenum wires of 2.0 mm in diameter were used as a working and counter electrode, respectively. These molybdenum wires were encased in quartz tubes to prevent an electrical contact with other electrodes. One end of the molybdenum wires were polished thoroughly by using sand paper prior to every use. The Ag/Ag$^-$ reference electrode contains 1.00 mol% of AgCl in the LiCl-KCl eutectic melts and the Ag wire is inserted into the tube allowing the Ag wire being immersed in the molten salts. Finally, the top of the reference electrode was sealed with a Teflon tape to prevent an evaporation of the molten salts at high temperature.

The temperature of the molten salt was measured to ± 1°C using a calibrated K type Chromel-Alumel thermocouple wire. Cyclic voltammograms were obtained using a voltametric analyzer (Gamry Instruments Reference 600 potentiostat/galvanostat) interfaced with a PC at a scan rate of 50.0 mVs^{-1}. Electrochemical potentials were measured by using a electrometer (Keithley Model 6514, input impedance = 2×10^{14} Ω). All the performance and sample preparations were handled inside a glove box with argon atmosphere in which the oxygen content and moisture levels were less than 1 ppm.

Fabrication of Ag/Ag$^+$ reference electrodes. Three tube-based Ag/Ag$^-$ reference electrodes, (1) Pyrex tube with a thin wall-end (Py-REF), (2) quartz tube with a thin wall-end (Quartz-REF), (3) quartz tube with a tungsten tip junction (W-tip-Quartz-REF) were fabricated to test their performance for an ionic conduction and electrochemical measurement in LiCl-KCl eutectic melts in the temperature range between 400 to 700°C.

Pyrex and quartz tubes with a thin wall-end were prepared by using a general glass blowing technique. A W-tip-Quartz-REF was prepared by inserting a small piece of tungsten wire (1.0 mm diameter, 7.0 mm length) into the bottom wall of the quartz tube as shown in Fig. 2. Prior to the insertion, the surface of the tungsten metal tip was oxidized by using a torch flame in order to obtain a high ionic conduction through the porous tungsten oxide layer.

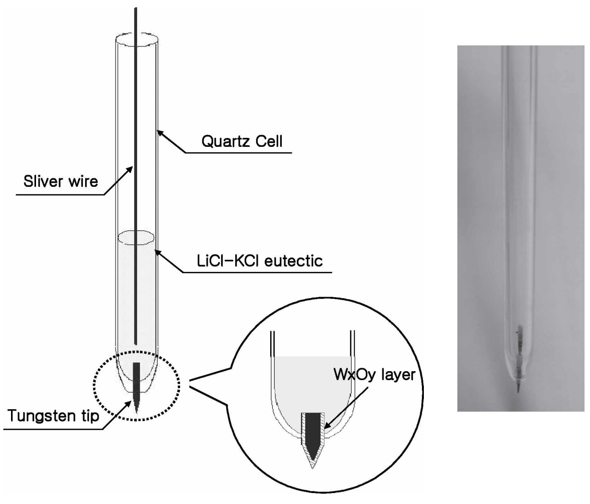

Figure 2. Conceptual diagram and photo of the quartz tube-based reference electrode with a tungsten tip junction.

Results and discussion

The electrochemical reaction of the Ag/Ag$^+$ reference electrode in molten salts can be described as follows:

$$Ag^- \text{ (molten salt)} + e^- \text{ (Ag wire)} = Ag \text{ (Ag wire)} \quad (1)$$

A conventional Pyrex tube-based reference electrode has been widely used since it has advantages such as a low cost and easy fabrication by a glass blowing technique. Since one end of the Pyrex electrode is inserted into a thin-wall, at approximately less than 0.5 mm, it provides a high ionic conduction due to a diffusion of the sodium ion in the Pyrex. Quartz fabrication into a thin end-wall is performed by using a hydrogen-oxygen flame as well as a glass blowing technique in our laboratory. Even though a precise mechanism of ionic conduction for a quartz tube-based reference electrode has not been established yet, the resistance of the quartz end-wall, which is mainly affected by the thickness of the end-wall, is too high to provide a sufficient ionic conduction at temperatures lower than 750°C. The required ionic conduction can be achieved by using a porous diaphragm or a salt bridge. For the same logical connection, a porous metal oxide layer was applied to our new design of a quartz tube-based electrode for an ionic conduction. Surface of a small piece of tungsten wire was oxidized by using a torch and then inserted into the bottom end of the quartz tube. Fig. 2 shows a conceptual drawing of the quartz tube-based Ag/Ag$^+$ reference electrode with a metal tip junction which contains a porous metal oxide layer for an ionic conduction as well as a photo of our final product.

Performance of three types of tube-based Ag/Ag$^+$ reference electrodes, a pyrex tube type, a quartz tube type, and a quartz tube with a tungsten tip junction were tested for their stability, and also their electrochemical properties. Fig. 3 shows the photos of three types of tube-based electrodes after a 12 hours experiment in LiCl-KCl eutectic melts at 750℃. The Pyrex tube-based electrode was severely damaged and finally broken to pieces probably due to its low melting point (820℃), while quartz tube-based electrodes revealed a good stability in a molten salt experiment at a high temperature.

Performance of the quartz tube-based reference electrode was tested by measuring the potential difference by using the Pyrex tube-based reference electrode as a primary reference. The potential difference between the quartz tube-based W-tip-Quartz-REF and the Pyrex tube-based Py-REF in the

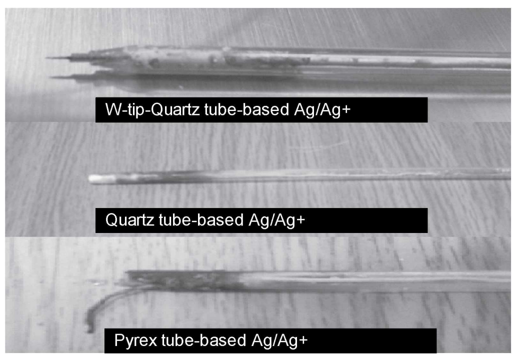

Figure 3. Shapes of the W-tip-Quartz-REF, Quartz-REF and Pyrex-REF after the electrochemical experiments at 750°C.

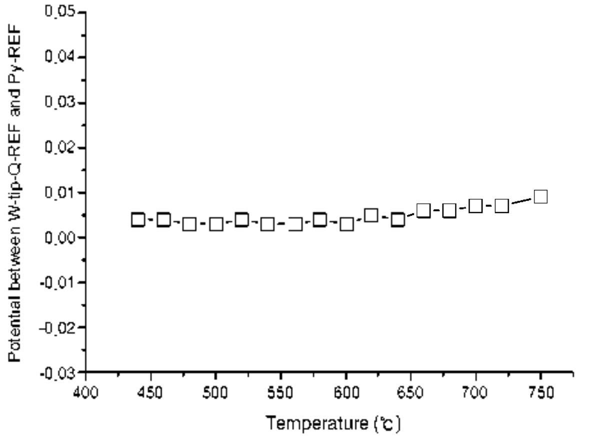

Figure 4. Electrochemical junction potentials between the quartz tube-based Ag/Ag^+ reference electrodes with a tungsten tip junction and the pyrex tube-based Ag/Ag^-reference electrode in the LiCl-KCl eutectic melt at various temperatures.

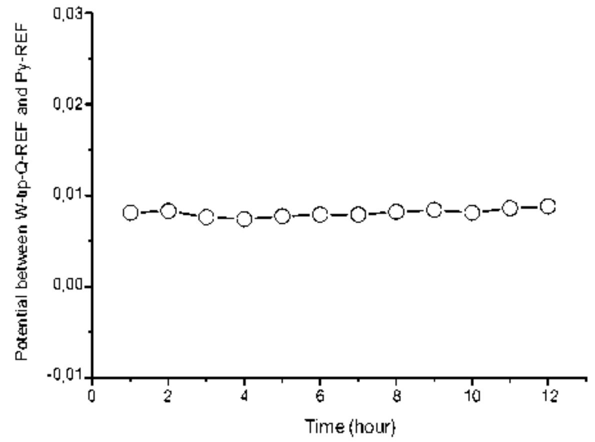

Figure 5. Electrochemical junction potential changes between the quartz tube-based Ag/Ag^- reference electrodes with a tungsten tip junction and the pyrex tube-based Ag/Ag^+reference electrode in the LiCl-KCl eutectic melt at 700 °C for various time durations.

LiCl-KCl eutectic melts were measured in the temperature range between 440 and 750°C. As shown in Fig. 4, a low potential difference of less than 10 mV was observed.

Stability of our newly designed W-tip-Quartz-REF was tested for 12 hours at 700°C. As shown in Fig. 5, the potential difference between the W-tip-Quartz-REF and the Py-REF one only varies within 1.4 mV, which indicates a good stability. In General, tungsten metal is oxidized to WO_3 in an oxygen atmosphere.[8] In this oxidation process, the surface of the tungsten wire turns to a porous structure due to the density difference of W metal (19.35 g/cm^3) and WO_3 (7.16 g/cm^3).[9] Therefore, it can be concluded that a good stability of the W-tip-Quartz-REF is mainly due to the porous structure of WO_3 formed on the surface of the tungsten wire, which provides additional ion conducting path.

Fig. 6 and Fig. 7 show representative examples of the cyclic voltammograms for the LiCl-KCl eutectic melts at the molybdenum electrode obtained with the W-tip-Quartz-REF and the quartz tube-based Ag/Ag^+ electrode (Quartz-REF), respectively, with in a temperature range between 450 and 700°C. Quartz-REF did not provide a stable and reproducible current response with a severe noise for the applied potential range between -2.5 and 0.5 V on the Mo working electrode at the temperature below 600°C as shown in Fig. 6. Even though this noise phenomenon became lower as the temperature increased, some noises were still observed at the temperature higher than 600°C. This result indicates that the Quartz-REF cannot be recommended as a reference electrode in the temperature range between 450 and 700°C.

It was found that the current increase at the beginning of potential scanning (0.5 V) and the vertex potential (-2.5 V) was increased as shown in Fig. 7. This phenomena happens prob-

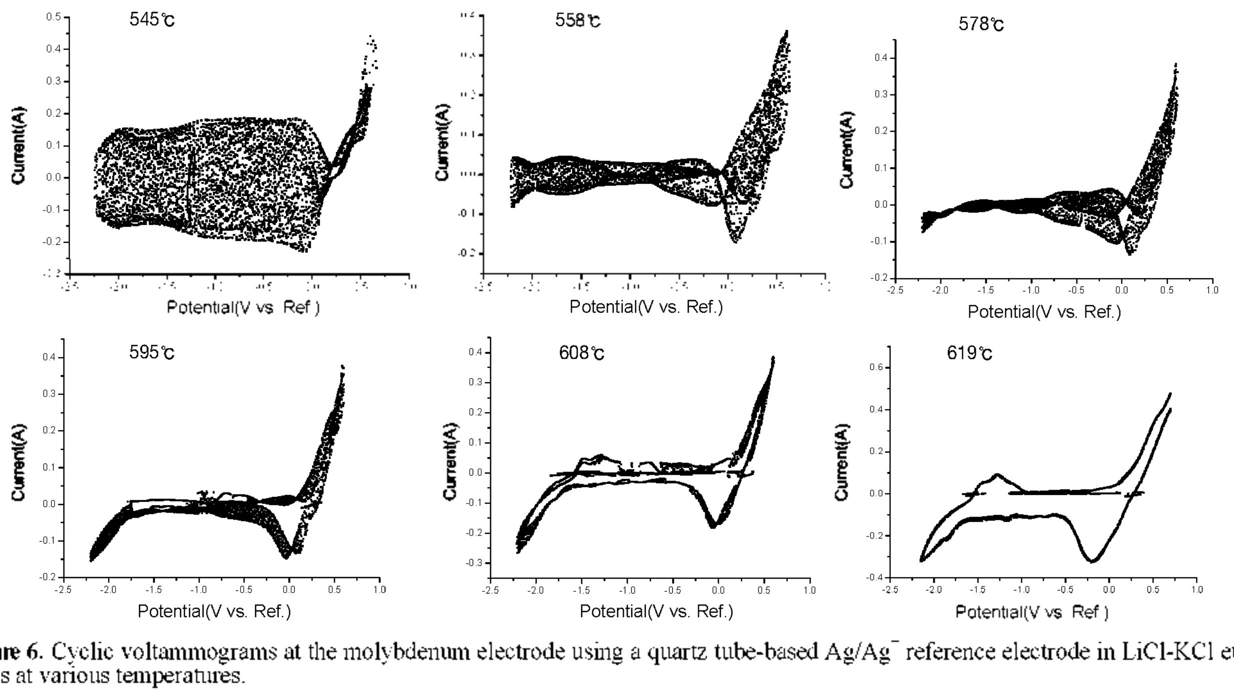

Figure 6. Cyclic voltammograms at the molybdenum electrode using a quartz tube-based Ag/Ag^- reference electrode in LiCl-KCl eutectic melts at various temperatures.

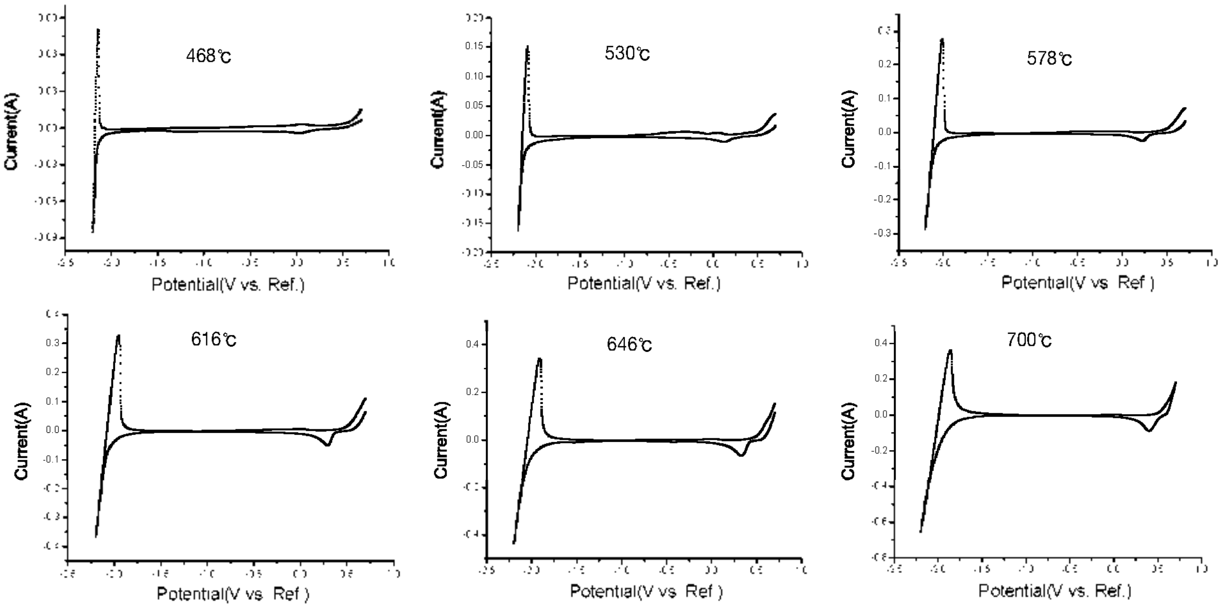

Figure 7. Cyclic voltammograms at the molybdenum electrode using a quartztube-based Ag/Ag^+ reference electrode with a tungsten tip junction in LiCl-KCl eutectic melts at various temperatures.

ably due to that the reaction rate of electrolyte oxidation (Li^+ + e → Li^-) and reduction (Cl^- → 1/2 Cl_2 + e) reactions were increased. The rate of electrochemical reaction, generally, increases exponentially rate with overpotential as well as the slope of the current gain.[10] Therefore, the polarization behavior shown in Fig. 7 seems to correspond to the normal electrochemical behavior of overpotential and temperature. However, when using the Quartz-REF, relatively smaller current responses, thus loss of current, were observed from the beginning (0.5 V) to the vertex (-2.5 V) potential under the same experimental condition. As the IR drop causes the loss of current, this result indicates a superiority of the W-tip-Quartz-REF with a point junction compared with the Quartz-REF from the IR drop of view.

Conclusions

In this study, we investigated the performance of a newly designed Ag/Ag^+ reference electrode in a quartz tube with a tungsten tip junction. The oxide layer on the surface of the tungsten metal tip provided a high ionic conduction. The results of the electrochemical potential measurements between the W-tip-Quartz-REF and the Py-REF one in the LiCl-KCl eutectic melts for a wide temperature range, and also a 12 hour experiment at 700°C, revealed a good performance and stability of our W-tip-Quartz-REF. The results of the cyclic voltammetry measurement indicated that the Ag/Ag^+ reference electrode in the quartz tube with a tungsten tip junction can provide a good performance for a wide temperature range, especially at a high temperature up to 700°C. Consequently, a quartz-tube based Ag/Ag^+ reference electrode with a tungsten tip junction can be a good solution for an electrochemical measurement for a wide temperature range in molten salts.

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