Preliminary study on the development of a quartz tube based reference electrode for electrochemical measurement in high temperature molten salts

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1. Introduction

Pyrochemical processing of nuclear fuels using a molten salt as a solvent is regarded as one of promising option for future spent nuclear fuel management concept.[1] Molten salts are known as suitable media for metal electrorefining and electrowinning. In order to reach a better understanding and control of the metal deposition processes, accurate knowledge of the electrochemical deposition mechanism is essential. Therefore, many elcctrochemical studies of actinides and lanthanides in various molten salts have been carried out in the past decade.[2,3]

In electrochemical studies, a three-electrode cell incorporating a stable reference electrode is essential to avoid uncertainty of the electrode reactions. The Ag/Ag^+ electrode is a conventional reference electrode used for molten salts media such as LiCl and LiCl/KCl eutectics. At molten salts temperature between 450 and 600℃, the pyrex, so called sodium glass, was commonly used as a reference electrode which can be easily fabricated into a thin-wall tube and thus gives a sufficient ionic conductivity. However, at temperature above 600℃, it cannot be used since it can be easily bent due to its low melting point. Quartz is commonly used in various research fields at high temperature up to 1200℃.

In this study, the Ag/Ag^+ reference electrode in quartz tube was fabricated with metal tip junction which contains porous metal oxide layer for ion conduction.

2. Result and Discussion

The electrode reaction of Ag/Ag^+ reference electrode in molten salts is as follows:

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

The conventional pyrex tube based reference electrode has been used widely since it has advantages such as low cost and easy fabrication by glass blowing technique. Since the one end of the pyrex electrode was fabricated into a thin-wall approximately less than 0.3 mm, it provides high ion conduction due to the diffusion of sodium ion in pyrex. However, pyrex based electrode cannot be used in molten salts of higher temperature above 600°C. A quartz tube based Ag/Ag^+ reference electrode was fabricated with metal tip junction which contains porous metal oxide layer for ion conduction. Fig 1. shows the pyrex tube based electrode after 12 hours experiment at 650°C and quartz tube based electrode after 24 hours experiment at 750 °C. the pyrex tube based electrode was deformed severely. Quartz is satisfactorily stable in molten salts at higher temperature.

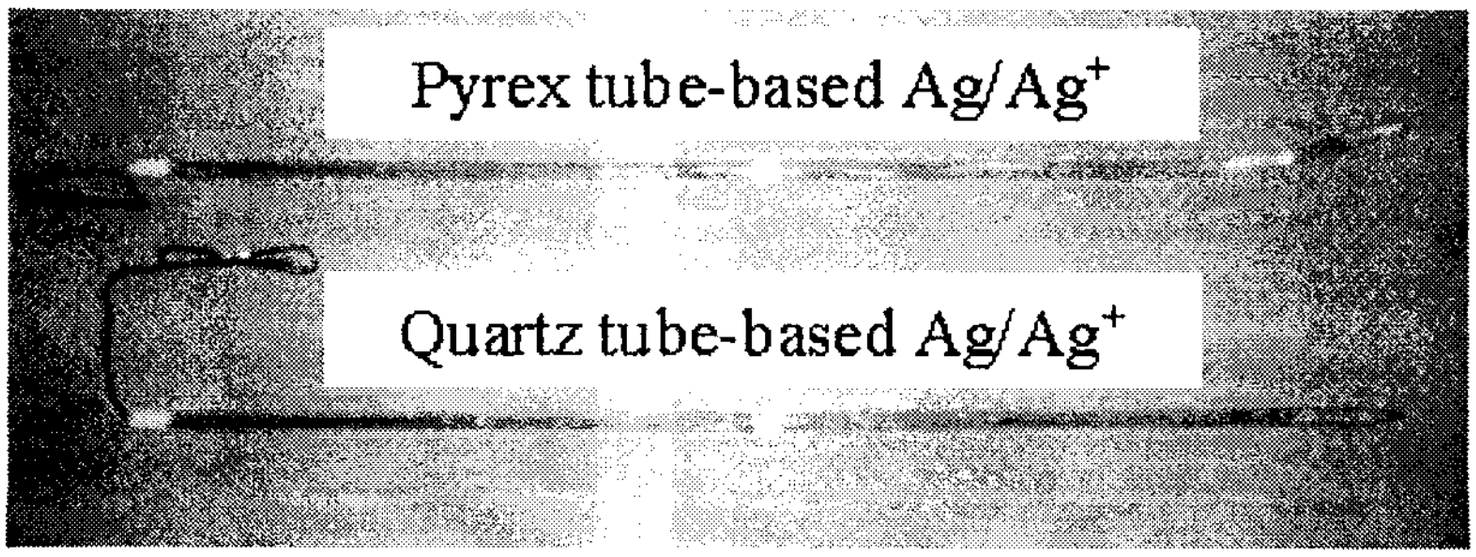

Fig. 1. Shapes of the Pyrex-REF and Quartz-REF after the electrochemical experiments at 750°C.

Performance of the quartz tube based reference electrode was tested by measuring a junction potential using the magnesia tube reference electrode as a primary reference. Electrochemical potentials of both the pyrex tube based (Pyrex-REF) and quartz tube-based Ag/Ag^+ reference electrodes (Quartz-REF) versus the MgO tube-based Ag/Ag^+ reference electrode (MgO-REF) in the LiCl-KCl eutectic melt were plotted in the temperature range between 425 and 750°C. As shown in Fig. 2, low junction potentials less than 10 mM were observed.

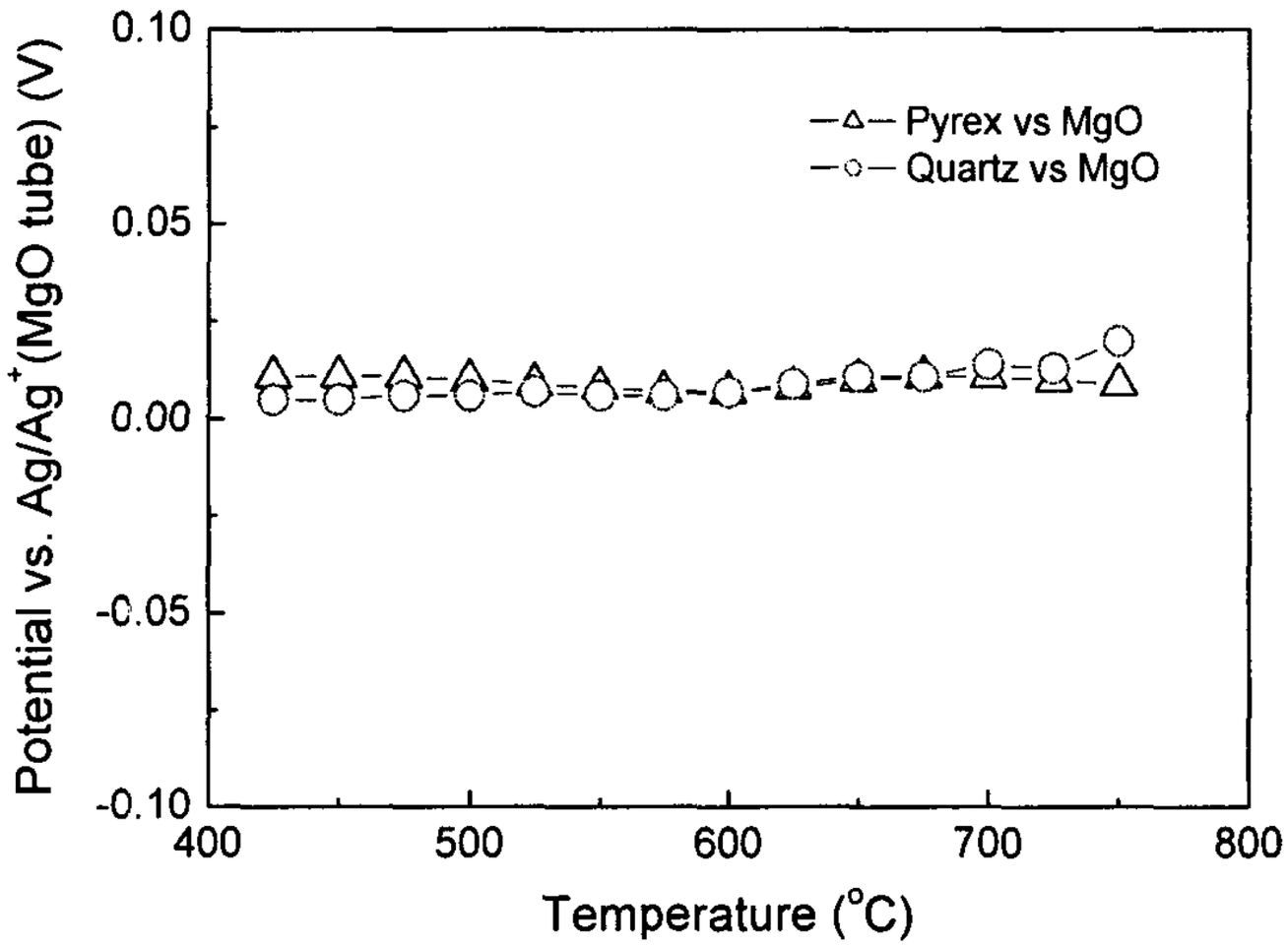

Fig. 2. Electrochemical potentials of both the pyrex tube based and quartz tube based Ag/Ag^+ reference electrodes versus the MgO tube-based Ag/Ag^+ reference electrode in the LiCl-KCl eutectic melt.

3. Conclusion

The Ag/Ag^+ reference electrode in quartz tube was fabricated with metal tip junction which contains porous metal oxide layer for ion conduction. Quartz is satisfactorily stable in molten salts at higher temperature above 600°C. Performance test of quartz tube based reference electrode was conducted by measuring a junction potential using the magnesia tube reference electrode as a primary reference. As a result, a quartz tube based Ag/Ag^+ reference electrode can be used for electrochemical measurement in high temperature molten salts.

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