Reference Electrode at Molten Salt: A Comparative Analysis of Electroceramic Membranes

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A reference electrode is important for controlling electrochemical reactions. Evaluating properties such as the reduction potential of the elements is necessary to optimize the electrochemical processes in pyroprocessing, especially in a multicomponent environment. In molten chloride systems, which are widely used in pyroprocessing, a reference electrode is made by enclosing the silver wire and molten salt solution containing silver chloride into the membranes. However, owing to the high temperature of the molten salt, the choice of the membrane for the reference electrode is limited. In this study, three types of electroceramic, mullite, Pyrex, and quartz, were compared as reference electrode membranes. They are widely used in molten salt electrochemical processes. The potential measurements between the two reference electrode systems showed that the mullite membrane has potential deviations of approximately 50 mV or less at temperatures higher than 650℃, Pyrex at temperatures lower than 500℃, and quartz at temperatures higher than 800℃. Cyclic voltammograms with different membranes showed a significant potential shift when different membranes were utilized. This research demonstrated the uncertainties of potential measurement by a single membrane and the potential shift that occurs because of the use of different membranes.

Keywords: Mullite, Pyrex, Quartz, Open circuit potential, Mechanical properties

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1. Introduction

During electrochemical processes for treating radioactive waste, a reference electrode is essential to measure electrode potentials and control electrochemical reactions at a working electrode, particularly under a multi-component environment. A pseudo reference electrode (i.e., a metal rod or wire) is a common choice for the molten salt pyroprocessing at higher than 500℃ [1]. A platinum or silver wire is widely used for such a purpose. However, the pseudo reference electrode has a lack of thermodynamic equilibrium due to no common component (anion or cation) in the two adjacent phases. The potential of the reference electrode itself keeps changing according to applied current densities [2].

To overcome these issues, several researchers have adopted different electroceramics including mullite [3-6], Pyrex [7-10] quartz [11, 12], Vycor [7, 8], Supermax [13], and alumina [14]. The electroceramics physically isolate a reference electrode from high-temperature bulk molten salts while providing a conductive connection. Over 400℃, there are only a few choices for electroceramic membranes. Among electroceramics, a range of acceptable temperature differs. The operating temperatures of pyroprocessing are 500℃ for LiCl-KCl eutectic salt and 650℃ for LiCl salt [15-17]. Pyrex is an applicable membrane for 500℃, but it becomes not acceptable for 650℃ since it undergoes a solid-state phase transition [18]. It is still ambiguous under which conditions different electroceramics are suitable for the membranes of reference electrode systems. There is no information about what potential errors arise from the choices of different electroceramics while converting measured values from one reference electrode system to another. Most of the previous studies have adopted a single reference electrode system without comparing different ones under the same conditions.

This study aims at providing a practical guideline to choose appropriate electroceramic membranes for experimental conditions in molten salt pyroprocessing. We compared the characteristics and performances of three commonly used electroceramics, which are mullite, Pyrex, and quartz, at a range of temperatures in LiCl-KCl [5, 6]. In all experimental cases, the electroceramic membranes contain an Ag wire immersed in a few weight percent of AgCl dissolved in LiCl-KCl. We collected, analyzed, and compared various material properties such as mechanical strength, thermal conductivity, electrical conductivity, and phase diagram. We compared the reproducibility and stability of measured potentials as well as the required time to reach equilibrium when initially heating an electrochemical cell.

2. Criteria of Ideal Reference Electrode System

A successful reference electrode system needs to satisfy the following requirements:

1. An electrochemical reaction on the reference electrode should be electrochemically reversible;
2. The electrode potential of the reference electrode should remain stable without noticeable change;
3. The electrode potential of the reference electrode should be immediately returned to the initial equilibrium potential if the current passes through the reference electrode;
4. The repeated cycles of varying temperature should not cause potential hysteresis at the reference electrode system;
5. The structural materials should have enough mechanical strength while not being dissolved in the liquid phase of electrolyte;
6. The reference electrode system should have a liquid junction or Donnan potential as low as possible [19].

The choices of electroceramics are essential to meet the last three criteria. The selection criteria of the reference electrode membranes at a given range of temperature include:
1. Electrical conductance;
2. Potential stability;
3. Mechanical strength;
4. Phase stability;
5. Fast initial equilibrium.

To ensure sufficient electrical conductance and stable measured potentials, the impedance of electroceramics should not exceed 4 kΩ under experimental conditions [19]. Higher impedance produces more noise in electrochemical signals. By considering mechanical strength and phase stability, the membrane should not undergo a phase change and should not be damaged by thermal shocks at operating temperature. Besides, the potential deviation should be within the range of 10 mV during long-term measurements [19]. Practically, the initial equilibrium of the open circuit potential has to be reached in a fast manner. Last, the production of reference electrode systems should be reproducible and uncomplicated, so that the size and the design can be readily modified.

Under room temperature, several successful reference electrode systems are meeting these requirements. They include the saturated calomel electrode (SCE; Hg/Hg₂Cl₂/Cl⁻), the Ag/AgCl electrode (Ag/AgCl/Cl⁻), the Hg/Hg₂SO₄ reference electrode (Hg/Hg₂SO₄/SO₄²⁻), and the Hg/HgO reference electrode (Hg/HgO/OH⁻). Under a system of molten chloride salt, a Cl₂/Cl⁻ reference electrode system is a standard electrode system like a standard hydrogen electrode (SHE) under aqueous solutions. Similar to the SHE, it is difficult to maintain and use this easy reference electrode system in an actual experiment.

3. Experimental Setup

3.1 Potential Materials for Reference Electrode Membrane: Mullite, Pyrex, and Quartz

This study adopts three different electroceramics: mullite, Pyrex, and quartz. Mullite is a mixture of alumina and silica (3Al₂O₃·2SiO₂ or 2Al₂O₃·SiO₂). Mullite is manufactured by combining alumina with silica via sintering. It has the advantage of high strength with excellent thermal shock resistance [15]. Pyrex is a type of glass mainly composed of borosilicate (SiO₂ and B₂O₃) with sodium oxide (Na₂O) and alumina (Al₂O₃). It is commonly used as a reference electrode membrane at a temperature range from 450~500℃ due to its easy fabrication and sufficient ionic conductivity. Quartz is a crystalline mineral of silica (SiO₂) with high mechanical strength and a low thermal expansion coefficient. Mullite is optically opaque, while Pyrex and quartz are transparent.

3.2 Preparation of Electrochemical Cells

For a reference electrode system, an Ag wire (99.999%, Alfa Aesar) of 1 mm diameter was used as an electrode. The Ag wire was immersed in LiCl (44wt%)-KCl (56wt%) eutectic containing a few weight percent of AgCl. As shown in Fig. 1, both electrode and electrolyte for the reference electrode system were housed in a thin-walled electroceramic membrane. A mullite membrane has an inner diameter of 3 mm, an outer diameter of 5 mm, and a length of 350 mm. Both Pyrex and quartz membranes have an inner diameter of 3 mm, an outer diameter of 5 mm, and a length of 350 mm.
2 mm, an outer diameter of 4 mm, and a height of 350 mm. Tungsten rods (99.99%, Alfa Aesar) of 1 mm diameter were used as a counter electrode and a working electrode. Working and counter electrodes were partially protected with quartz tubes to above the level of the electrolyte in order to avoid direct contacts among metal electrodes. An electrochemical cell was made of a closed-end quartz tube and was inserted into and heated within the furnace. The electrochemical cell has an inner diameter of 25 mm and a height of 350 mm as shown in Fig. 2.

All metallic electrodes were polished by 600-grit silicon carbide papers and then were cleaned with ultrapure water for 1 hour in an ultrasonic washing machine. This procedure was repeated using 1200-grit silicon carbide papers. Then, the metallic electrodes were dried in a vacuum oven for more than 12 hours. The salt mixtures of LiCl-KCl eutectic (99.99%, anhydrous, Sigma Aldrich), AgCl (99.99%, anhydrous, Sigma Aldrich), and CoCl₂ (99.99%, anhydrous, Alfa Aesar) were used. All molten salts were first dried at 200°C for 5 hours to remove all possible moisture in the salt.

### 3.3 Electrochemical Apparatus and Furnace System

All electrochemical measurements were performed using a PARSTAT 4000A potentiostat /galvanostat (the Princeton Applied Research). The electrochemical tests were carried out in a glove box under an inert Argon atmosphere where the concentrations of moisture and oxygen were maintained at 1 ppm or less. A high-temperature reaction chamber made of type 304 stainless steel was located at the bottom of the glove box. The reaction chamber was surrounded by a ceramic heater with a programmable temperature controller. A water cooling was applied to the interface between the furnace and the glove box.

### 3.4 Electrochemical Measurements

Several electrochemical measurements were performed in this study. First, an open circuit potential was measured between two identical reference electrode systems for an electrode, an electrolyte, and a membrane at different temperatures of 500, 650, 800°C, to check the stability and reproducibility of potential at these temperatures. Second, an
open circuit potential was measured between two reference electrode systems with different membranes. For the open circuit potential measurements between the two reference electrode systems, the potential differences are measured until the cell reached the equilibrium voltage with a standard deviation of less than 5 mV in the last 10 minutes. The electrolytes used in reference electrode systems were prepared from the same batch of well-mixed electrolytes with careful treatments. These two reference electrode systems are inserted into an electrochemical cell. Third, cyclic voltammetry was performed at 650℃ with LiCl-KCl-CoCl₂ (0.5wt%) for different membranes with a scan rate of 0.5 V/s. For the cyclic voltammetry measurement, a tungsten rod was used as both working and counter electrodes, and the signal was measured one day after the target temperature was reached. Fourth, the potential difference between the two reference electrodes with different AgCl concentrations was measured with the Pyrex membrane.

4. Results and Discussion

4.1 Mechanical Strength and Phase Stability

Mechanical strength is crucial to maintain the physical boundaries of electroceramic membranes. Moreover, phase transitions will change many mechanical properties and, thus, physical shapes. Regarding the mechanical strength, Young’s modulus and thermal conductivity are important properties. Table 1 shows these two properties for three electroceramic materials [20-27]. Young’s modulus is defined as the uniaxial stress divided by the strain or the deformation. Higher Young’s modulus means more resistance to the external force, so the stretching of the material is minimized. The thermal conductivity affects the thermal shock resistance. Higher thermal conductivity causes more excellent thermal shock resistance of the material. Since pyroprocessing operates at 500–650℃, thermal shock from careless handling can damage the reference electrode system with rapid increases and decreases in temperature.

The solid-state phase transitions of membranes can limit the range of operating temperatures for reference electrode systems. Fig. 3 shows the shapes of mullite, Pyrex, and quartz tubes after they were immersed in LiCl-KCl at temperatures up to 800℃. While both mullite and quartz tubes did not show any external damages, the Pyrex tube was severely deformed after exposing at 650℃. Its phase transition can explain the severe physical deformation of Pyrex. The phase diagram of mullite, Pyrex, and quartz are shown in Fig. 4 [23, 28, 29]. The phase boundaries of
mullite and Pyrex changes by their material compositions. On the other hand, quartz is made of a single component of SiO₂. The lowest solidus temperatures of mullite and quartz are respectively about 1600 and 1700 °C at the atmospheric pressure, which means that it does not undergo a phase change at the operating temperature of pyroprocessing. As shown in the phase diagram of Pyrex, it starts to melt from 450°C partially (i.e., solidus temperature) and becomes liquid completely at about 800°C (i.e., liquidus temperature). Pyrex still works perfectly fine at 500°C, but it is not recommended to use at a temperature higher than 600°C.

4.2 Open Circuit Potential Measurements using Reference Electrode Systems

Ideally, the potential difference should be zero when it is measured between the two identical reference electrodes. During electrochemical experiments, an ideal reference electrode does not participate in electrochemical reactions, and thus, the current does not flow through the reference electrode. In reality, the tiny amounts of electric current can flow to the reference electrode at high-temperature molten salt environments [4]. For this reason, it was found to have a potential difference of tens of mV to over 100 mV depending on operating temperatures and the electrical resistance of membranes [5, 11]. The deviations from the ideal behaviors are because of the ohmic drops across bulk electrolytes and the Donnan potentials across membranes. In the case of high temperature molten salt with high electrical conductivity in the range of several S/cm, the ohmic drop across the electrochemical cell with an inner diameter of 25 mm is almost negligible, so the Donnan potential across the two membranes is the main potential difference. \( \Delta E = \Delta E_{\text{donnan}} + \Delta E_{\text{ohmic}} + \Delta E_{\text{donnan}} \approx 2\Delta E_{\text{donnan}} \)

4.2.1 Initial Equilibrium of the Reference Electrodes Depending on Membrane Types

Fig. 5 shows the open circuit potentials measured across two Ag wires immersed LiCl-KCl-(1wt%) AgCl enclosed in the same electroceramics. Mullite was measured at 650°C, Pyrex at 500°C, and quartz at 500 and 800°C. Fig. 5a shows that the mullite membrane requires about 10 hours to reach the equilibrium potential at 650°C. Fig. 5b shows that the Pyrex membrane reaches equilibrium almost immediately from the beginning of the measurement. Fig. 5c shows that the quartz membrane requires 7 hours to
stabilize at 500℃, and it requires less than 2 hours to reach
equilibrium at 800℃.

The results at 500℃ show that Pyrex reaches equilibri-
um potential faster than the quartz membrane, which means
that Pyrex is more suitable at 500℃ than quartz. Quartz
membrane requires less time to reach equilibrium at its tar-
get temperature. Quartz at 800℃ requires only two hours to
reach equilibrium while it requires almost 10 hours to reach
equilibrium at 500℃. The results imply that the quartz
membrane shows better performance at 800℃ than 500℃.
Mullite requires about 10 hours to reach equilibrium po-
tential at its target temperature, which is much longer than
the target temperatures of the other two membranes. The
potential difference between the two reference electrodes
at the equilibrium cell voltage is compared in section 4.2.2.

4.2.2 Open Circuit Potential Measurements across
the Same Reference Electrode Systems

Fig. 6 shows the potential difference and its noise mea-
sured across two Ag wires immersed LiCl-KCl-(1wt%) AgCl
enclosed in the same electroceramics. The difference was obtained during the last 10 minutes of the quasi-
equilibrium defined in Fig. 5. The noise of the potential
difference is compared with the standard deviation of the
potential differences.

In the case of mullite membranes, the potential differ-
cence decreases as temperature increases. The mullite mem-
brane reaches the open circuit potential about 146 mV at
500℃, 110 mV at 650℃, and 60 mV at 800℃. The standard
deviation of the potential is less than 0.5 mV at all tempera-
ture ranges. On the other hand, the Pyrex membrane shows
an increasing potential difference as temperature increases
as Pyrex goes through a phase transition from solid to par-
tially liquid state at about 600℃. This trend is in the oppo-
site direction from those of mullite and quartz that do not
have phase transitions. At about 500℃, the open circuit po-
tential measured for the Pyrex membrane has about 50 mV
with a noise smaller than 0.1 mV. The quartz membrane has
a potential difference of about 20 mV at 800℃, where it
has substantially decreased from 280 mV at 500 and 650℃.
The noise of the potential difference of quartz has substan-
tially decreased to about 0.1 mV at 800℃ compared to 500
and 650℃. This result implies that a quartz membrane can
be used at temperatures higher than 800℃.

For the cases of mullite at higher than 650℃, Pyrex at
all temperatures, and quartz at higher than 800℃, measured
redox potential values from reference electrode systems
have possible errors about 10-50 mV occurring from the
Donnan potential of a single reference electrode. The standard deviations of the potential difference are less than 0.5 mV for the temperature ranges suggested. Combining the results from Fig. 3 and phase diagram from Fig. 4, mullite might be suitable to use as the reference electrode membrane at temperatures higher than 650 ℃, Pyrex at temperatures under 500 ℃, and quartz at temperatures higher than 800 ℃ for the high temperature molten salt electrochemistry.

### 4.2.3 Open Circuit Potential Measurements across Different Membranes of Reference Electrode Systems

The potential difference of the reference electrodes with different membranes and its noise are plotted in Fig. 7. The potential difference of the two reference electrode systems with Pyrex and quartz membrane was not performed, since the operating temperature range of the Pyrex and quartz membrane deduced in section 4.2.2 was significantly different. The potential difference of mullite vs. Pyrex at 800 ℃ was not measured due to the mechanical failure of the Pyrex membrane at the high temperature shown in Fig. 3.

The open circuit potential measurements show that there is a significant difference in the potentials. From Fig. 7a, there is about 354 mV of a potential difference between the mullite and quartz membrane at 500 ℃, 341 mV at 600 ℃, and 242 mV at 800 ℃. The noise is significantly decreased at 650 ℃ and 800 ℃ compared to 500 ℃, which agrees with the applicable temperature range suggested from section 4.2.2. From Fig. 7b, there is about 353 mV of the potential difference between the mullite and Pyrex membrane at 500 ℃, and 342 mV at 650 ℃. The standard deviation shows similar values at both temperatures.

Recalling the results from 4.2.2, the magnitude of the potential differences with different membranes is much higher than that with the same membranes. As stated in section 1, previous studies have adopted only a single reference electrode system to measure the electrochemical properties and not compared with two or more reference electrode systems with different membranes. The results from Fig. 7 imply that the different membranes can shift the potential measurement values significantly. The type of reference electrode membrane should be clearly stated during the potential measurements, and the relationship of the reference electrode potential using different membrane needs to be identified if the experiment is performed with different types of reference electrode membranes. The difference in the potential measurement due to the difference in the membrane is expressed in section 4.3.
4.3 Cyclic Voltammetry Measurement of CoCl₂

The cyclic voltammetry (CV) using the cobalt chloride is shown in Fig. 8 and Fig. 9. The concentration of cobalt chloride was 0.5wt% and 1wt% of AgCl solution was used, and the reduction peak potential was observed. The CV was performed at 650°C using mullite, Pyrex, and quartz membrane, which is shown in Fig. 8. The cyclic voltamgram at 650°C shows that mullite is the most suitable membrane to be used at this condition, while Pyrex shows
the distortion of the signal near the reduction and oxidation peaks and quartz shows sharp noise peaks at all potential ranges. Also, the reduction peak potential shows significant differences when different membranes are utilized. Mullite shows reduction peak potential of -0.068 V, Pyrex of about -0.2 V, and quartz of about -0.14 V. The differences in the reduction peak potential is much larger than the accepted experimental error of about 50 mV. This shows that the differences in the membrane can affect the quantitative potential measurements.

The cyclic voltammetry at the target temperatures of each membrane was performed. The cyclic voltammograms of mullite at 650°C, Pyrex at 500°C, and quartz at 800°C are shown in Fig. 9. The reduction peaks of mullite at 650°C, Pyrex at 500°C, and quartz at 800°C are -0.068, -0.246, and -0.11 V (vs. 1wt% Ag/Ag⁺) respectively.

The shift in the reduction peak potential of Co²⁺/Co was investigated. The apparent reduction potential (E₀') for the reversible insoluble reaction using the Ag/Ag⁺ reference system can be expressed as follows [10]:

\[
E_0' = E_p - \frac{RT}{nF}\ln(X_{Cu^2+}) - 0.08540 \frac{RT}{nF} + E_0^{AgCl} + \frac{RT}{F}\ln(X_{Ag^+})
\]

(1)

where \(E_p\) is the reduction peak potential, \(R\) is the universal gas constant, \(T\) is the absolute temperature, \(n\) is the number of electrons participated in the reaction, \(F\) is the Faraday constant, and \(X_{m^n}\) is the mole fraction of the metal species (M) in the solution. The apparent reduction potentials of mullite at 650°C, Pyrex at 500°C, and quartz at 800°C are calculated to be -1.157, -1.298, and -1.237 V (vs Cl₂/Cl⁻). The apparent reduction potential can be expressed with the standard reduction potential (E₀) as follows:

\[
E_0' = E_0 + \frac{RT}{nF}\ln(\gamma_{Cu^2+})
\]

(2)

where \(\gamma_{Cu^2+}\) is the activity coefficient of the Co²⁺. If the potential difference coming from the different membrane is ignored, then the changes in the apparent reduction potential due to the temperature change can be expressed as follows if the activity coefficient remains constant:

\[
E_{T_2}^{0'} - E_{T_1}^{0'} = (E_{T_2}^0 - E_{T_1}^0) + \frac{R(T_2 - T_1)}{nF}\ln(\gamma_{Cu^2+})
\]

(3)

The potential difference between the apparent reduction potentials at different temperatures are affected by two terms. The first term is the change in the standard reduction potential. The standard reduction potential values at 500, 650 and 800°C are -1.14, -1.054, and -0.977 V (vs Cl₂/Cl⁻) respectively [30]. The second term related to the activity coefficient is affected by the change in the temperature. The activity coefficient of Co²⁺ was assumed in the order of 10⁻³ [31]. Substituting these conditions, the temperature increase of 150°C will decrease the redox potential by 0.045 V.

According to the calculations from the above equations, the increase in the temperature from 500°C to 650°C should increase the apparent reduction potential by about 0.041 V. However, the CV results of 500°C using the Pyrex membrane and 650°C using the mullite membrane showed a decrease of -0.140 V, which shows a huge difference from the theoretical calculation. The theoretical calculation did not include the potential deviation coming from the membrane difference, so the difference of membrane should have affected the huge difference. The results from section 4.2.3 show that the mullite and Pyrex membrane can have a potential difference as large as 0.353 V, which can explain the potential shift of the two cyclic voltammograms.

The results of the CV at 650°C using the mullite membrane and at 800°C using quartz membrane show a similar trend. Theoretically, the apparent reduction potential should increase by about 0.032 V when the temperature increases from 650°C to 800°C. However, the potential increases by 0.061 V, which is larger than the theoretical calculations. Quartz at 800°C can have a potential deviation of 0.01 mV, and mullite at 650°C can have that of 0.055 mV which is shown in section 4.2.2. This deviation accounts for the additional potential decrease when the temperature is
increased from 650°C to 800°C. The cyclic voltammograms imply that the difference in the reference electrode membrane can affect the redox potential values significantly.

The results from sections 4.2 through 4.3 shows consistent results on the appropriate temperature range of each material. The open circuit measurements between the two reference electrode systems suggested the applicable temperature for each membrane. The reference electrode with the mullite membrane showed decreasing potential deviations at temperatures higher than 650°C. Pyrex showed the least potential deviation at 500°C, and quartz at 800°C. Therefore, mullite is suitable as a reference electrode membrane at temperatures higher than 650°C. Pyrex at temperatures lower than 500°C, and quartz at temperatures higher than 800°C. The cyclic voltammogram of CoCl₂ also supported the suitable temperatures of each membrane. Also, using different membrane material can shift the potential value which can be observed from sections 4.2.2 and 4.3. Further analysis of the numerical derivation of the potential difference coming from different membrane material needs to be investigated to convert the experimental values where the different membrane is used.

4.4 Potential Difference with Different AgCl Concentrations in the Reference Electrode Solution

In the molten chloride electrochemistry, 1wt% of AgCl [4,7,9,10] and 1mol% of AgCl [14, 32, 33] concentration in the reference electrode solution is widely adopted. Therefore, the potential difference of the reference electrodes with 1wt% AgCl concentration and 1mol% AgCl concentration was measured using the Pyrex membrane. The potential difference between the different AgCl concentrations shows 64.4 mV, which is close to the theoretical value of 61.2 mV using the Nernst equation. Therefore, a potential shift of 61.2 mV should be considered when converting the potential values from 1wt% AgCl to 1mol% AgCl.

5. Conclusion

This research has tried to suggest the appropriate electroceramics for molten salt electrochemical processes and reveal whether the usage of different membrane material for the reference electrode in the molten salt media affects the quantitative electrochemical measurements. The properties of the mullite, Pyrex, and quartz as high temperature reference electrode membranes are compared in terms of their mechanical and electrochemical properties. The comparison of the mechanical properties and the electrochemical measurements show that the membranes have different applicable temperatures and the utilization of the different membrane material significantly affects the quantitative potential measurements. This research has shown the uncertainties coming from using a reference electrode membrane, the potential difference when different membranes are utilized, and the quantification of the potential shifts with different membranes.

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