

CHAPTER III

EXPERIMENTAL

In order to construct the LiFe_5O_8 electrode and test its potential reproducibility and stability, lithium ferrite has been synthesized by means of a solid state reaction at high temperature. Next, the solidification step is applied so that this compound can be coated onto a medium which allows measurement of its potential. Several potentiometry techniques were applied to check its validity and stability such as Open circuit potential measurement and cyclic voltammetry. Both these techniques were applied under room temperature and high temperature conditions. This confirms that this LiFe_5O_8 electrode can be operated functionally in both conditions.

3.1 Reagents

All reagents were of analytical-reagent grade. Deionized water was of resistivity $> 17 \text{ MOhm} \cdot \text{cm}^{-1}$. Lithium carbonate (Li_2CO_3) with $>99\%$ purity and ferric oxide, red-anhydrous hematite were obtained from Sigma Aldrich and Fisher Scientific respectively. Lithium metaborate (LiBO_2) was obtained from SPC Science. The ceramic crucibles were obtained from COORS (USA). The 0.5 mm diameter platinum wires were supplied by Fisher Scientific.

3.2 Method

3.2.1 Preparation of Lithium Ferrite (LiFe_5O_8) by Solid State Reaction

Lithium ferrite (LiFe_5O_8) was prepared by mixing fine Fe_2O_3 and Li_2CO_3 powder in a ceramic mortar with a $\text{Fe}_2\text{O}_3:\text{Li}_2\text{CO}_3$ ratio of 1:1. During the mixing procedure, a small amount of pure ethanol was added to help homogenize the mixture which was ground until the ethanol had completely evaporated. The sample was put in a ceramic crucible and dried in the furnace at 100°C for 1 hour followed by roasting in air at a temperature of 1100°C for 6 hours. At this point, two different forms of product were produced, one adhered to the side of crucible while the other

was contracted and concentrated at the centre of the crucible. The portion in the centre was found to be LiFeO_2 while the outer portion, which adhered to the crucible, contained some alumina. From the literature, LiFeO_2 is said to be an intermediate product of LiFe_5O_8 , thus Fe_2O_3 was again added to the LiFeO_2 removed from the first step at a ratio of 2:1 ($\text{Fe}_2\text{O}_3:\text{LiFeO}_2$) and mixed in the mortar as before. The sample was again dried in the furnace at 100°C for 1 hour and then roasted in air at 900°C and 1100°C for 3 and 6 hours respectively. Following are the expected reactions that occur in this stage:



After this second roasting in the furnace, an extraction process was applied to remove some contaminants from the product in the crucible. The extraction solution contained 1M HNO_3 and deionized water in the ratio of 1:4. The solution was poured over and vigorously stirred through the sample. After the extraction process, the sample was rinsed once again with deionized water to thoroughly remove the nitric acid. This was ensured by measuring the pH after each rinse. The sample was again dried in the furnace at 100°C for half an hour and left to cool to room temperature. A physically homogeneous gray powder was obtained.

3.2.2 LiFe_5O_8 Coating Process

There are many different ways to coat a compound onto a different medium. One of the methods is called a dip coating process. Basically, the medium (a platinum wire) was immersed into the hot molten compound so that the compound may adhere onto the wire. Due to the difference in temperature between the compound and the surroundings, a rapid cooling is achieved, forming a solid compound coated onto the medium. This was done by homogeneously mixing lithium metaborate (LiBO_2) with LiFe_5O_8 in different ratios (2:1, 1:1 and 1:2) in order to lower the melting point of the ferrite. The thoroughly mixed compounds were put into a ceramic crucible and roasted in the furnace at 1100°C for 15 minutes

as shown in Figure 3.1. Meanwhile, the platinum wire was prepared by polishing its surface with 400-grit sand paper and rinsing with acetone to remove soils and greases and coiled to produce a larger surface area for coating. Next, the crucible was taken out of the furnace and the platinum coil was delicately dipped into the molten lithium ferrite/metaborate mixture. This had to be done gently so that the molten ferrite totally and uniformly coated onto the coil. After a few seconds, the compound was solidified on the platinum wire in air. Consequently, a black, shiny lithium ferrite successfully adhered onto the platinum wire.

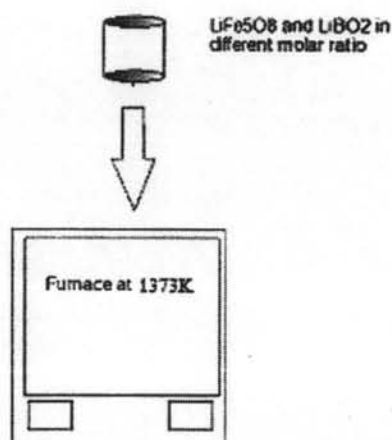


Figure 3.1 Schematic diagram for lithium ferrite coating process.

3.3 Electrochemical Measurements

A three electrode system was used for potential and polarization measurements of the lithium ferrite in known concentrations of lithium carbonate and lithium hydroxide solutions. The three electrodes consisted of LiFe_5O_8 on platinum wire which acted as the working electrode, the reference electrode used in this experiment is a standard calomel electrode and finally, a coiled platinum wire is used as the counter electrode. Along with the system, a potentiostat (Solartron 1286 Electrochemical Interface, Schlumberger) was used to control the parameters in this experiment. It also provided continuous data acquisition and potential determination over a period of time with connection to a computer controlled by CorrWare

software. This software has a variety of functions that can be applied in this work such as open circuit potential, potentiostatic function which is used in polarization experiments and cyclic voltammetry. These techniques were used to determine the potential stability and mechanism validation of the lithium ferrite electrode reaction as described in the previous chapter.

3.3.1 Open Circuit Potential Measurement (Room Temperature)

The potential was measured under different lithium ion concentrations obtained from the different lithium based compounds. The concentration of lithium carbonate and lithium hydroxide were chosen to be 10^{-3}M , 10^{-4}M and 10^{-5}M . This concentration range dictates the value of lithium ion in nuclear coolant systems which do not exceed 3ppm or approximately 10^{-4}M .

The open-circuit potential was measured for stability of LiFe_5O_8 in different lithium concentrations. As its name implies, there is no current conducted within this experimental system, therefore the potential drop is minimal and it is a measure of the equilibrium or mixed potential of the reaction. Figure 3.2 shows the experimental setup for a typical open-circuit potential measurement.

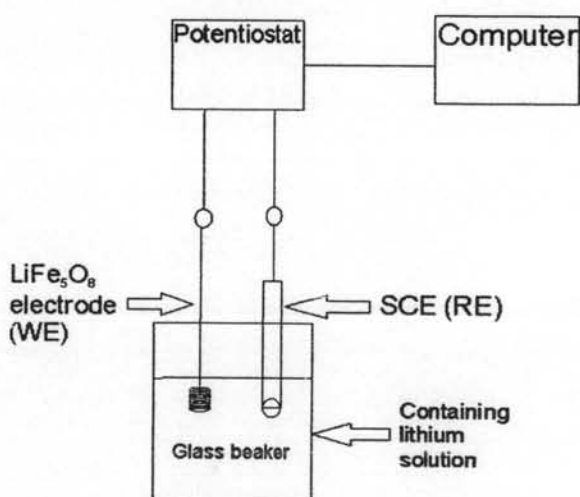


Figure 3.2 Schematic diagram for open circuit potential setup.

The electrochemical potential may be affected by the pH of the system as well as the ion concentration in the solution via the Nernst equation; in the first case, lithium ion concentration was considered. It is required to vary one of the parameters while keeping the others constant, so that the effect to electrochemical potential from that parameter can be clearly seen. At a starting point, the pH was kept constant by introducing an ammonium chloride buffer solution while adding a compound such as lithium chloride (LiCl) in order to vary the lithium concentration in the system. Considering a low pH system ($\text{pH} \approx 5.03 \pm 0.03$), where ammonium chloride was used as the buffer solution. The NH_4^+ ion will dissociate and react with the OH^- in water, thus the pH of the system should be maintained upon adding additional salts. An appropriate amount of LiCl was added to vary the lithium concentration since the addition of LiCl should not affect the pH of the system. In the high pH system ($\text{pH} \approx 8.75 \pm 0.03$), LiOH was used instead of NH_4Cl . Since a trace amount of LiCl was added into the LiOH solution, the pH of the system was maintained while varying the lithium concentration. These calculations are shown in Appendix A.3. The potential of the lithium ferrite was measured in each solution in the same manner as described before.

3.3.2 Cyclic Voltammetry Measurement (Room Temperature)

Cyclic voltammograms were obtained with the Solartron 1286 Electrochemical Interface (Schlumberger). In cyclic voltammetry, the potential is swept over a wide range causing a current to flow between the working electrode and counter electrode. Figure 3.3 shows the schematic diagram of three electrode system.

Before and after the cyclic voltammetry experiments, the open-circuit potential was measured to ensure the stability of LiFe_5O_8 potential as well as its consistency. Several measurement techniques were provided by the potentiostat as following;

- Applying different scan rates as low as 1 mV/s and as high as 20 mV/s
- Potential sweeping from positive to negative direction and vice versa

- Data acquisition interval (for example, 1 point per second or 1 point every 10 seconds)
- Polarization measurement or potentiodynamic measurement

This can be done automatically with the CorrWare software.

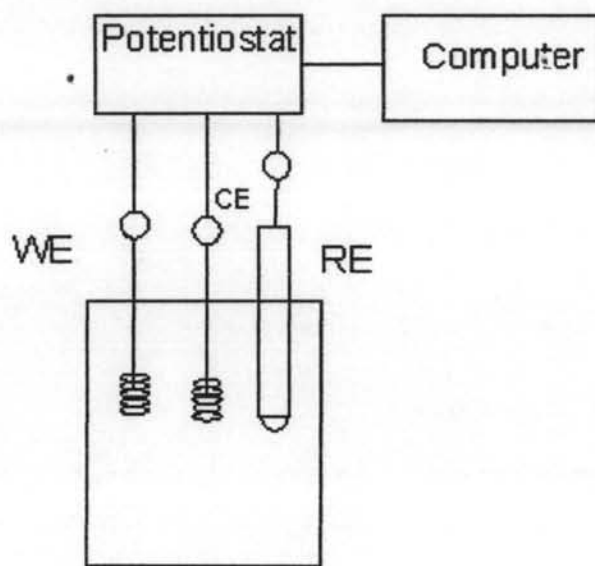


Figure 3.3 Experimental setup for cyclic voltammetry measurement on lithium ferrite coated platinum wire.

3.3.3 Open Circuit Potential and Cyclic Voltammetry Measurement (High Temperature)

The LiFe_5O_8 electrode was also tested in the titanium autoclave at high temperatures and high pressures where three-electrode system was applied. The experimental conditions were at temperatures between 25°C and 300°C and pressures between 0 psi and 1500 psi. The testing solution for this experiment was 10^{-4}M lithium hydroxide. This experiment determines the physical stability of LiFe_5O_8 in a stimulated nuclear coolant system environment as well as the chemical validity of this lithium ferrite electrode at high temperatures. The results obtained from this experiment will be compared with those at low temperature. Again, several electrochemical measurements were applied. For example, open circuit potential measurement and cyclic voltammetry were conducted to determine the potential

stability and reversibility of the lithium ferrite electrode respectively. The experimental schematic diagram is shown in Figure 3.4.

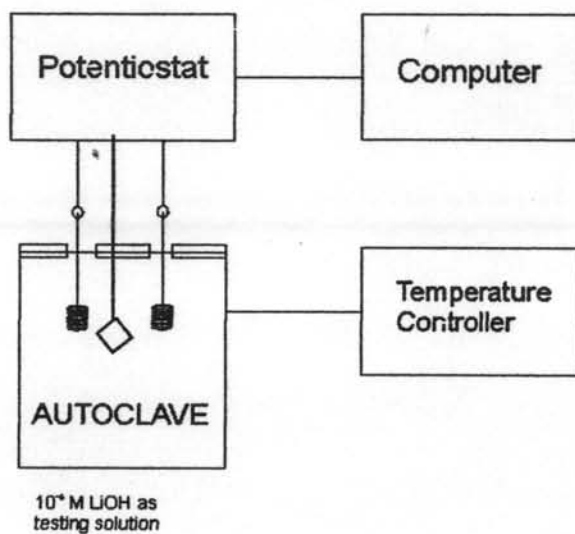


Figure 3.4 Schematic diagram for LiFe_5O_8 potential stability testing in autoclave at high temperatures and pressures.