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APPENDICES

Appendix A Calculations

A.1 Calculation of the Gibbs free energy to determine the Gibbs free energy of Fe₅O₇.

$$\Delta G^{\circ}_{LiFe_5O_8} = -2170.804 \text{ kJ/mol}$$

$$\Delta G^{\circ}_{Li} = -294 \text{ kJ/mol}$$

$$\Delta G^{\circ}_{H_2O} = -237.2 \text{ kJ/mol}$$

$$\Delta G^{\circ}_{Fe_2O_3} = -742.2 \text{ kJ/mol}$$

$$\Delta G^{\circ}_{Fe_3O_4} = -1015.4 \text{ kJ/mol}$$

From the proposed reaction; $LiFe_5O_8 + e^- + 2H^+ \rightarrow Li^+ + Fe_5O_7 + H_2O$

$$\Delta G^{\circ}_{rxn} = \sum \Delta G^{\circ}_{products} - \sum \Delta G^{\circ}_{reactants}$$

Take the Gibbs free energy of formation of reaction of equimolar ratio in $10^{-3}M$ LiOH, which is equal to -159.67 kJ/mol

$$\Delta G^{\circ}_{rxn} = \Delta G^{\circ}_{Li} + \Delta G^{\circ}_{Fe_5O_7} + \Delta G^{\circ}_{H_2O} - \Delta G^{\circ}_{LiFe_5O_8}$$

$$-159.67 = -294 - \Delta G^{\circ}_{Fe_5O_7} - 237.2 + 2170.804$$

$$\Delta G^{\circ}_{Fe_5O_7} = -1799.27 \text{ kJ/mol}$$

When compare the calculated of the Gibbs free energy of Fe₅O₇ with the Gibbs free energy of Fe₂O₃ and Fe₃O₄, they are very close.

A.2 Calculation for number of electrons transfer in 10^{-3}M LiOH at cathodic reaction.

$$|E_{pc} - E_{pc/2}| = \frac{47.7}{(\alpha n_a)}$$

$$|-577 + 210| = \frac{47.7}{(\alpha n_a)}$$

$$(\alpha n_a) = 0.13$$

From

$$i_p = (2.99 \times 10^5) n (\alpha n_a)^{1/2} A C D^{1/2} \nu^{1/2}$$

where

$$i_p = 1.32 \times 10^{-4} \text{ A}$$

$$A = 1.512 \text{ cm}^2$$

$$C = 1 \times 10^{-6} \text{ mol / cm}^3$$

$$D_{Li} = 1.03 \times 10^{-5} \text{ cm}^2 / \text{s}$$

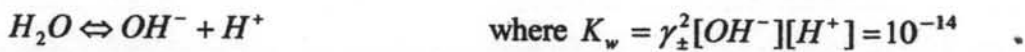
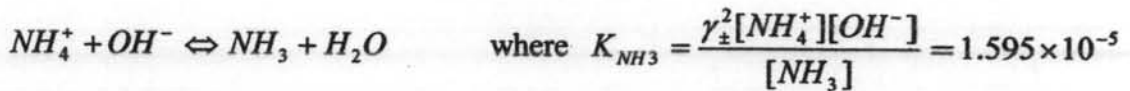
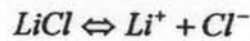
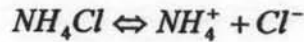
$$\nu = 20 \times 10^{-3} \text{ V / s}$$

hence,

$$n = 1.78 \approx 2$$

A.3 Determination of pH of the system which buffer solution was used.

A.3.1 Low pH system: consider 0.5M NH_4Cl and assume total dissolution



For convenient γ_{\pm} is assumed to be 1 first

From charge balance;

$$[\text{NH}_4^+] + [\text{H}^+] + [\text{Li}^+] = [\text{Cl}^-] + [\text{OH}^-]$$

$$[\text{NH}_4^+] = [\text{Cl}^-] + [\text{OH}^-] - [\text{H}^+] - [\text{Li}^+]$$

From total number of mole;

$$[\text{NH}_{\text{Total}}] = [\text{NH}_4^+] + [\text{NH}_3]$$

$$[\text{NH}_3] = [\text{NH}_{\text{Total}}] - [\text{NH}_4^+]$$

$$[\text{NH}_3] = 1 - [\text{NH}_4^+]$$

Substitute $[\text{NH}_4^+]$ and $[\text{NH}_3]$ into K_{NH_3} and write it as a function of $[\text{H}^+]$ as follow;

$$K_{\text{NH}_3} = \frac{\left(\frac{K_w^2}{[\text{H}^+]^2} + \frac{K_w}{[\text{H}^+]} - K_w \right)}{[\text{H}^+] - \frac{K_w}{[\text{H}^+]}}$$

Solve for $[\text{H}^+] = 2.5 \times 10^{-5}$ hence $\text{pH} = -\log[\text{H}^+] = -\log[2.5 \times 10^{-5}] = 4.6$

Then other parameters can be found accordingly

$$[\text{OH}^-] = 4 \times 10^{-14}$$

$$[\text{Cl}^-] = 1$$

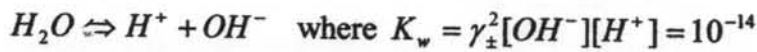
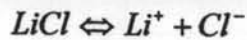
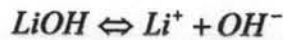
$$[\text{NH}_4^+] = 0.999975$$

$$[\text{NH}_3] = 2.5 \times 10^{-5}$$

$$\text{Since } \ln \gamma_{\pm} = \frac{-0.5\sqrt{I}}{1+1.5\sqrt{I}} \quad \text{where } I = \frac{1}{2} \sum z_i C_i$$

Substituting z_i and C_i , hence solve for γ_{\pm} . After obtaining activity coefficient, substitute back and recalculate for activity coefficient until it converges.

A.3.2 High pH system: consider 10^{-3} M LiCl added into 10^{-5} M LiOH and assume total dissolution



From the charge balance;

$$[\text{H}^+] + [\text{Li}^+] = [\text{Cl}^-] + [\text{OH}^-]$$

$$[\text{H}^+] + [\text{LiCl}] + [\text{LiOH}] = [\text{LiCl}] + \frac{K_w}{\gamma_{\pm}^2 [\text{H}^+]}$$

$$[\text{H}^+]^2 + [\text{LiOH}][\text{H}^+] - \frac{K_w}{\gamma_{\pm}^2} = 0$$

Solve for $[\text{H}^+] = 9.999 \times 10^{-10}$ hence $\text{pH} = -\log[9.999 \times 10^{-10}] = 9$

Other parameters can be calculated;

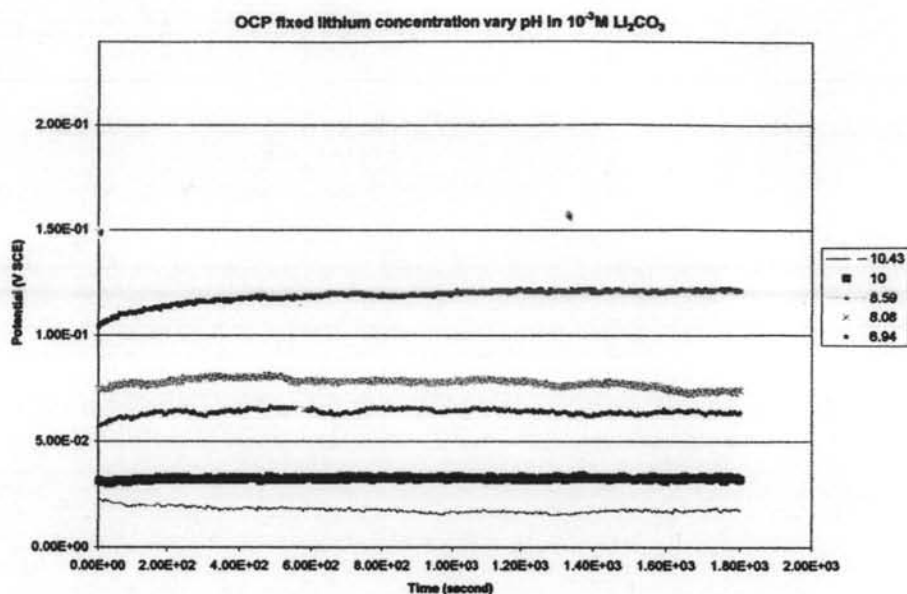
$$[\text{OH}^-] = 1 \times 10^{-5}$$

$$[\text{Li}^+] = 1.01 \times 10^{-3}$$

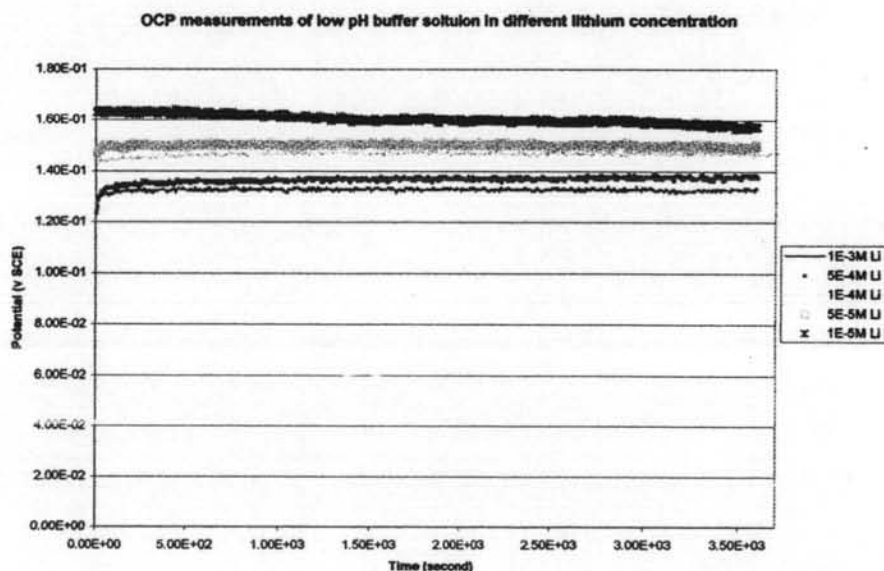
$$[\text{Cl}^-] = 1 \times 10^{-3}$$

The same procedure as applied for low pH calculation was applied to calculate the activity coefficient until it converges.

Appendix B Figures

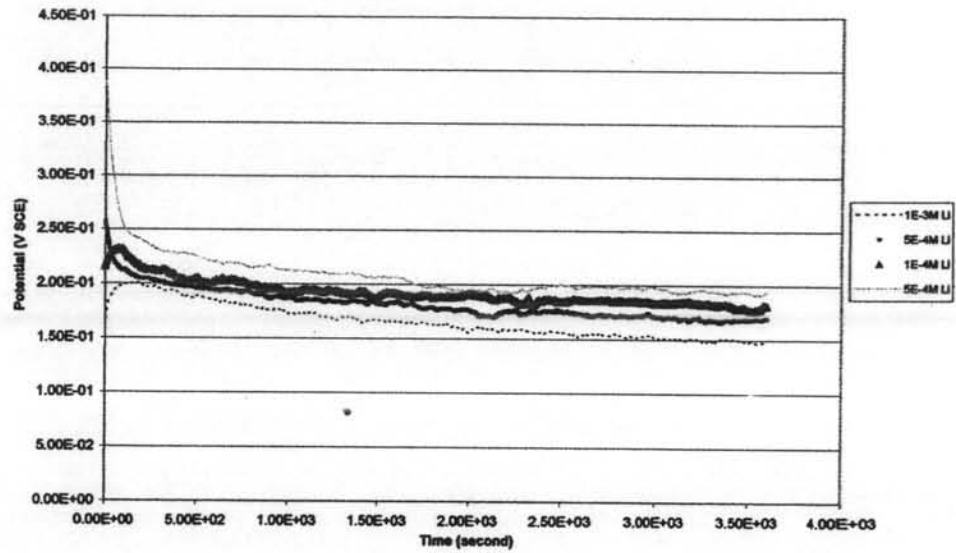


B.1 Open circuit potential measurement in $10^{-3}\text{M Li}_2\text{CO}_3$ solution where pH was varied by adding trace amount of hydrochloric acid.

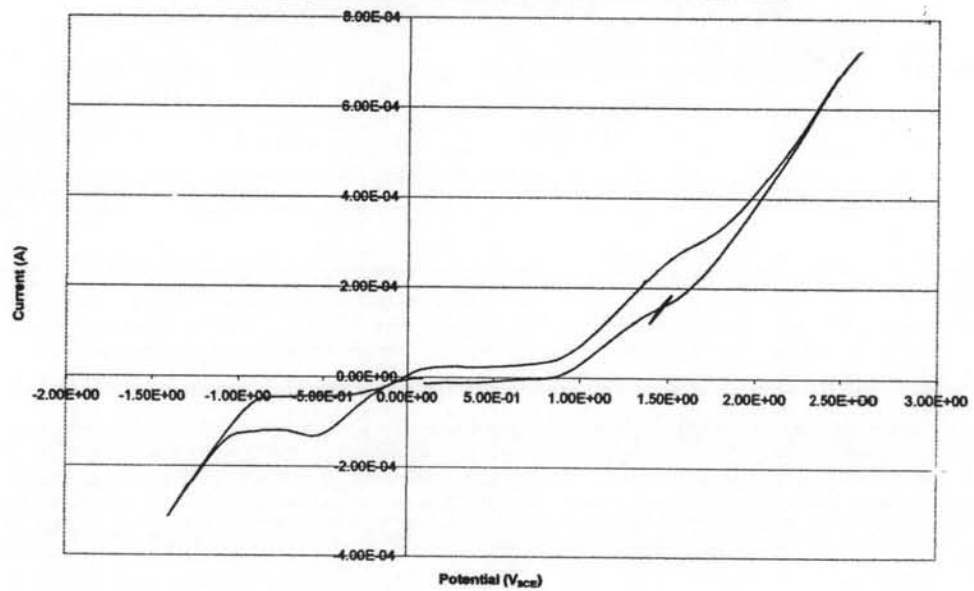


B.2 Open circuit potential measurement in NH_4Cl buffer solution at different lithium concentrations.

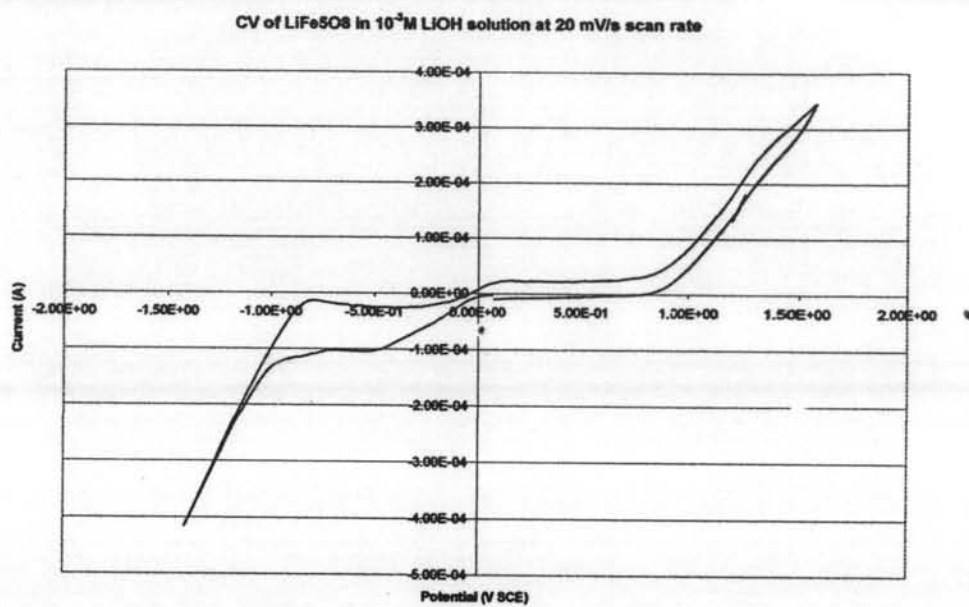
OCP measurements of high pH buffer solution with different lithium concentrations



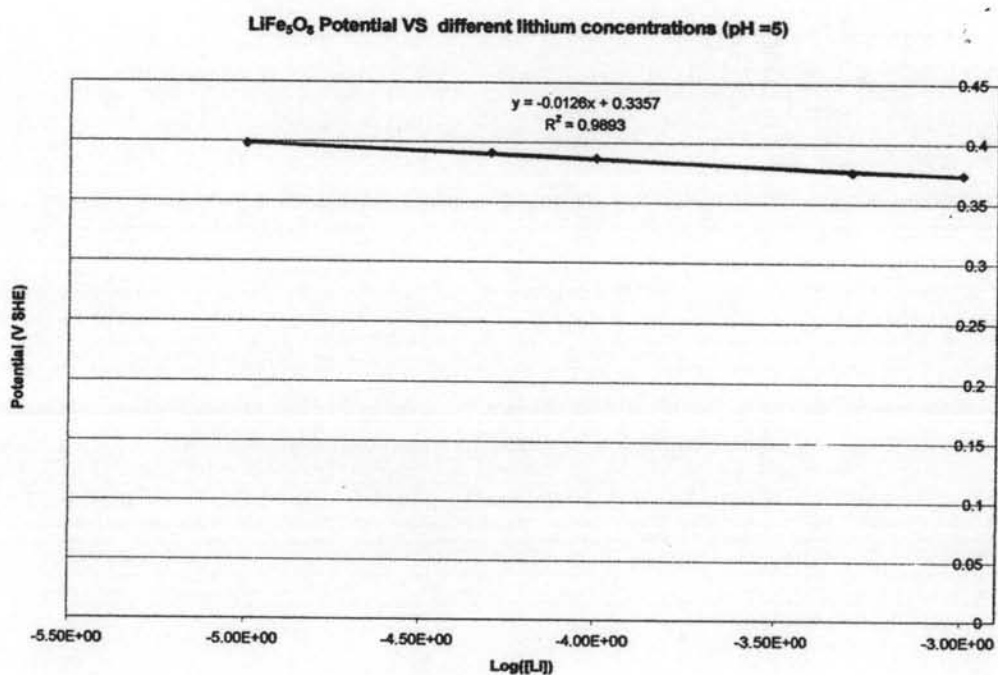
B.3 Open circuit potential measurement in LiOH and LiCl buffer solution at different lithium concentrations.

CV of LiFe_5O_8 in 10^{-3}M LiOH solution at 20 mV/s scan rate

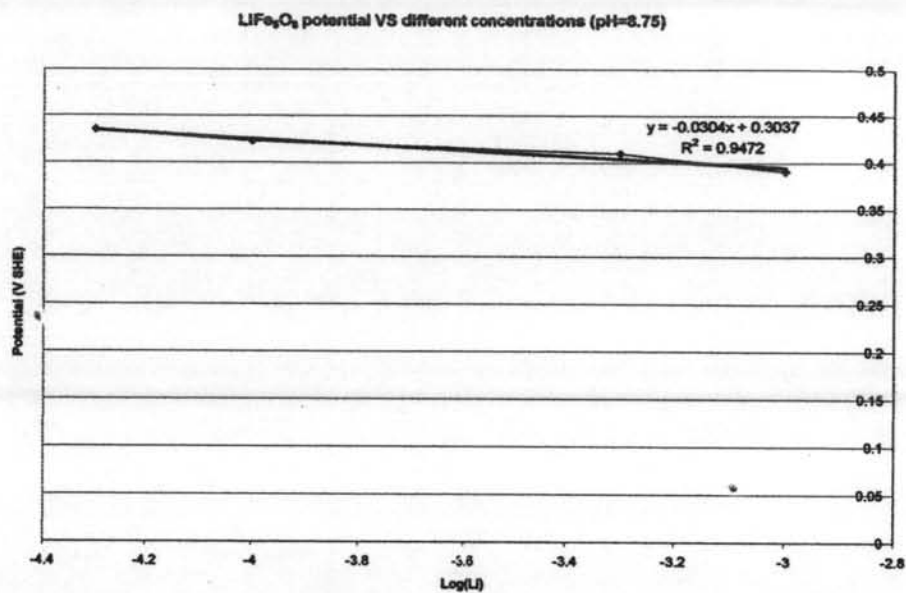
B.4 Cyclic voltammetry of LiFe_5O_8 electrode in 10^{-3}M LiOH at 20 mV/s scan rate.



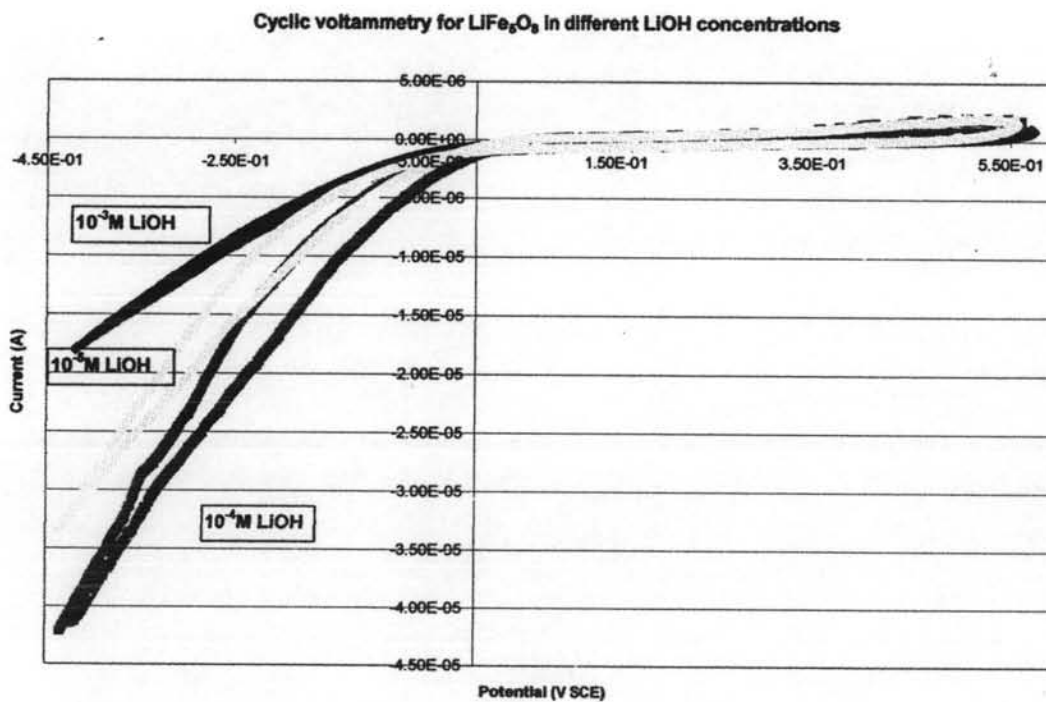
B.5 Another cyclic voltammetry of LiFe_5O_8 electrode in 10^{-3}M LiOH at 20 mV/s scan rate.



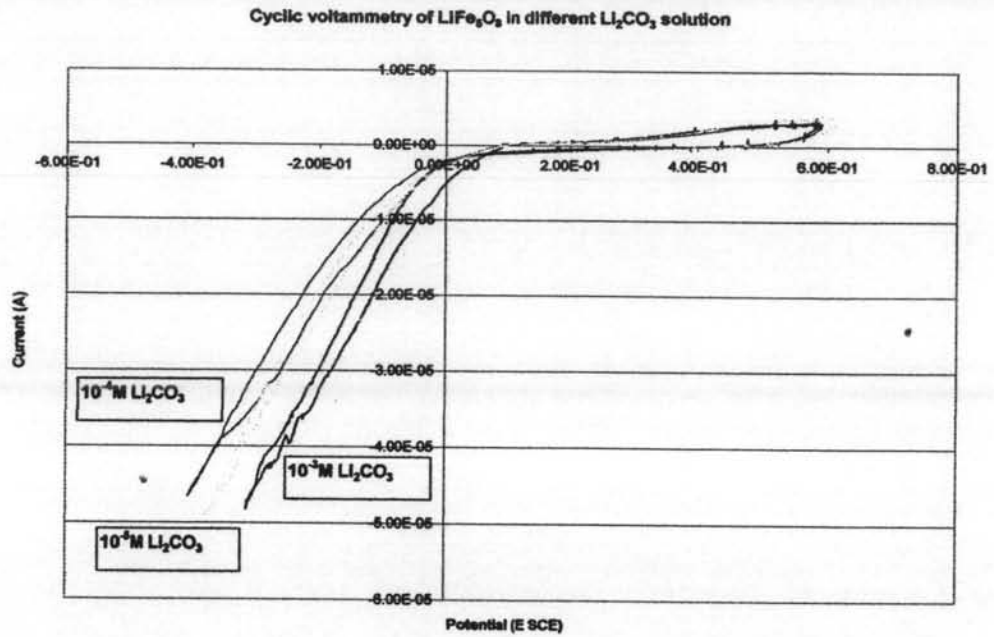
B.6 Potential VS logarithmic of lithium concentrations in NH_4Cl system (low pH).



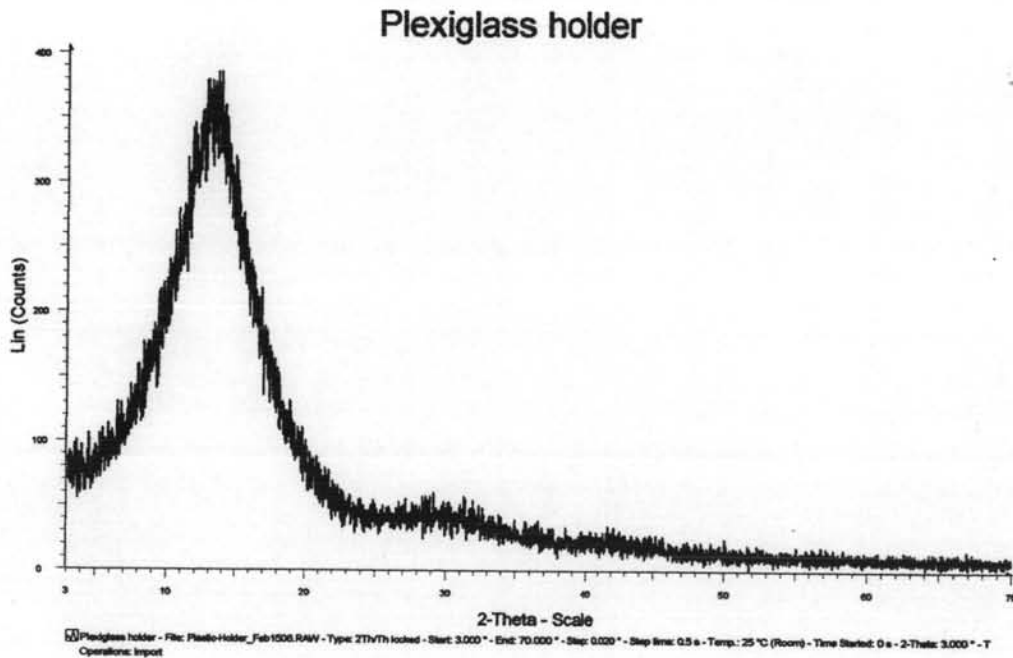
B.7 Potential VS logarithmic of lithium concentrations in LiOH with addition of LiCl system (high pH).



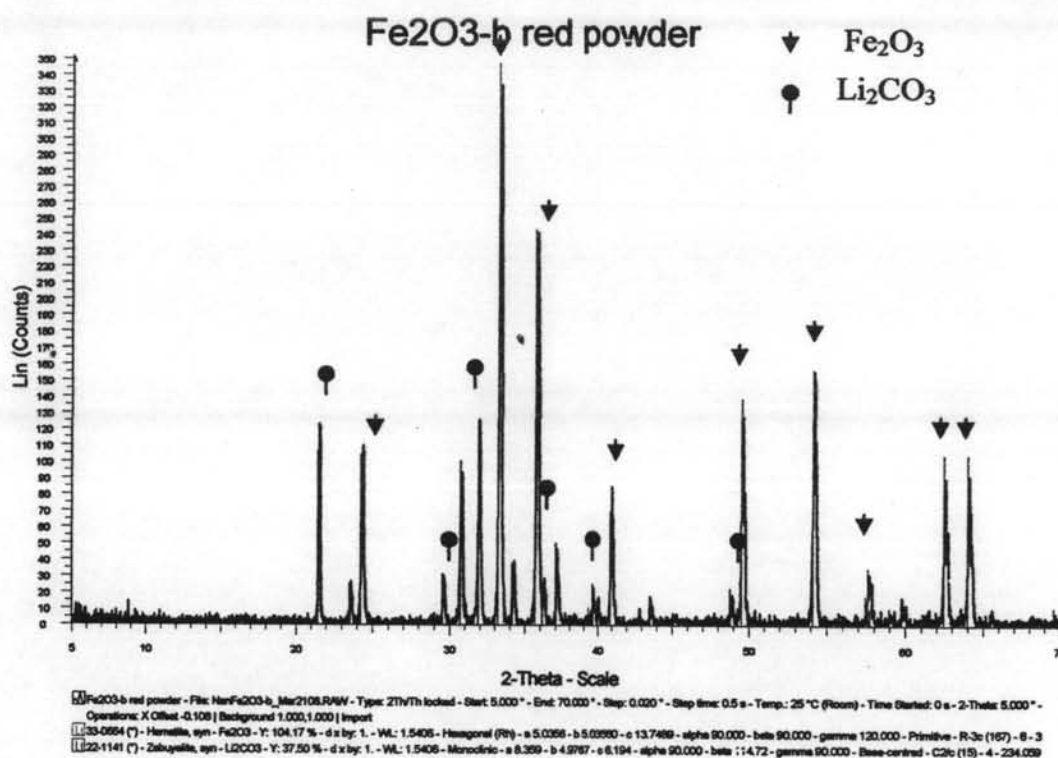
B.8 Cyclic voltammetry of LiFe₅O₈ in different LiOH concentrations.



B.9 Cyclic voltammetry of LiFe_5O_8 in different Li_2CO_3 concentrations.



B.10 XRD pattern of plexi glass sample holder.



B.11 XRD pattern of Li₂CO₃ and Fe₂O₃ before roasting in the furnace.

