Study of Lithium Intercalation towards the Development of an Electrochemical Kinetic Model for Lithium/Copper Phthalocyanine Cell

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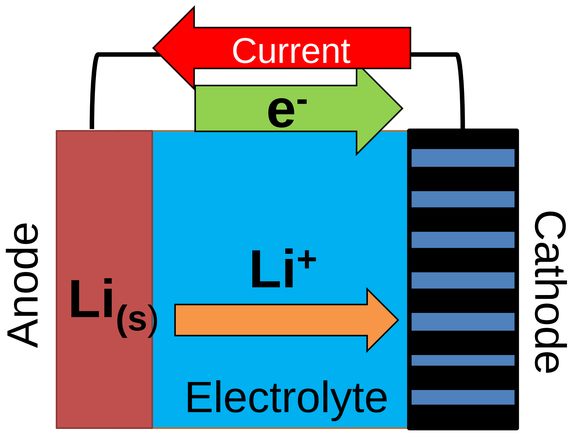
Introduction

The development of high capacity batteries is necessary to increase the viability of renewable energy sources by providing efficient storage of excess energy. Lithium ion batteries, with high charge storage capacity, are being further developed. Experimental investigations into high capacity cathode active materials have indicated that copper phthalocyanine is one such material. Some models have been developed to describe the observed cell behavior, but the system is not yet fully understood. To ensure that the model formulation will best describe observable data, a literature search into lithium intercalation was conducted.



Overall Reaction

$$Li^+ + e^- + S_v \rightleftharpoons (Li^+ - e^-) - S_{occp}$$

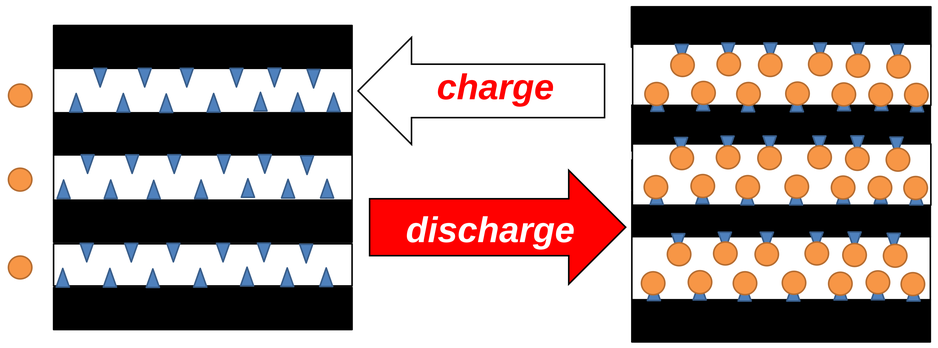
Considerations

- Intercalation host materials are typically anisotropic
- Active sites are treated as a reactant in place of the active material

Intrinsic Electrochemical Surface Reaction [1]

$$\mathrm{I^{tot}} = \mathrm{i_o A_s^t}\left[\frac{(\mathrm{X^{tot}} - \mathrm{X})^{1-\beta}(\mathrm{X})^{\beta}}{1+\alpha X}\right]\left[\mathrm{e}^{-\beta f \eta_s} - \mathrm{e}^{(1-\beta) f \eta_s}\right]$$

$$\mathrm{i_o} = \frac{M_{act} F}{\rho_o}\left(k_f^c C_{Li^+}\right)^{1-\beta}(k_b^a)^{\beta} \qquad f = \frac{F}{RT}$$

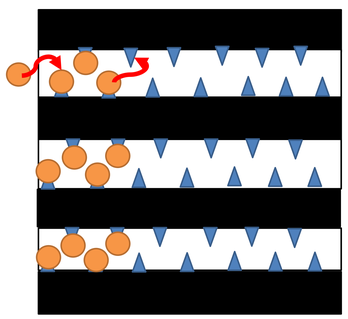


Transient Intercalation Wave Expression*

$$\frac{\partial X}{\partial t} = \frac{\mathrm{I^{tot}}}{\mathrm{A_s^t}} \exp\left[\frac{\mathrm{M_{act}}}{\rho_o}\left(\frac{1+\alpha X}{X^{tot}}\right)\left\{\frac{\sigma : \Delta\varepsilon - \beta\nabla\cdot\kappa\nabla(\mathrm{X}/\mathrm{X^{tot}})}{\mathrm{RT}}\right\}\right]$$

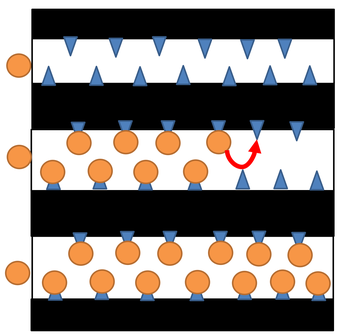
*Modified from [2]

Moving Reaction Front



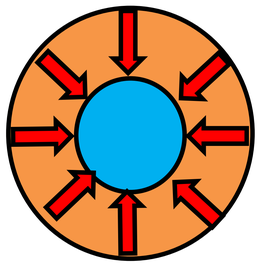
Anisotropic Bulk transport Limited

Intercalation Wave

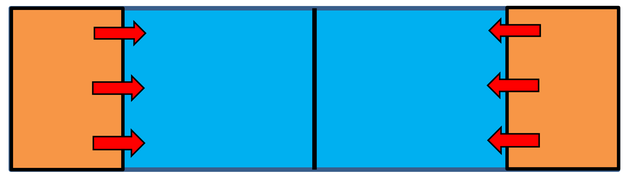


Anisotropic Surface Reaction Limited

Moving Reaction Front as Planar Shrinking Core



Shrinking Core Model: Reaction occurs at boundary between phases in a sphere



Moving Reaction Front Model: Similar to shrinking core with either a point of symmetry or impermeable material in place of center of a sphere

Recommendations

- Diffusion Limited: Limit diffusion effects with small particles; planar shrinking core model for internal diffusion
- Surface Reaction Limited: Requires more information to fit kinetic parameters

Select References

[1] Fellner, J.P., Sandhu, S.S. et al (2017). 2017 Annual LRIR Report, Appendix A, LRIR#: 16QCOR301

[2] Bazant, Martin Z. (2013) Accounts of Chemical Research 46 (5), 1144-1160

[3] G. Singh, D. Burch, and M. Z. Bazant, Electrochimica Acta 53, 7599 (2008).

[4] Froment et al. Chemical Reactor Analysis and Design, 3rd edition (2011), 252-259