Prospecting for Advanced Battery Materials

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Declaration

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. I give consent to this copy of my thesis, when deposited in the University Library, being made available for loan and photocopying subject to the provisions of the Copyright Act 1968.

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Timothy W. Jones
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I would like to dedicate this Thesis to the sentiment embodied in the following Carl Sagan quote.

"In science it often happens that scientists say, 'You know that's a really good argument; my position is mistaken,' and then they would actually change their minds and you never hear that old view from them again. They really do it. It doesn't happen as often as it should, because scientists are human and change is sometimes painful. But it happens every day. I cannot recall the last time something like that happened in politics or religion."

—Carl Sagan (1934–96), Astronomer.
Abstract

The electrochemical performance of a number of novel battery materials was investigated. These systems included the high-capacity primary alkaline AgCuO$_2$ cathode, the high-rate capable primary alkaline CuO cathode, and the secondary non-aqueous LiFe$_{1-y}$Mn$_y$PO$_4$ cathode.

AgCuO$_2$ samples are prepared via an aqueous co-precipitation route from Ag$^+$ and Cu$^{2+}$ nitrate salts, followed by chemical oxidation with sodium persulfate. The materials were tested as alkaline cathode materials for primary batteries in terms of their rate capabilities. AgCuO$_2$ discharges via four equivalent-charge reduction processes, via $\text{AgCuO}_2 \rightarrow \text{Ag}_2\text{Cu}_2\text{O}_3 \rightarrow \text{Ag}^0/\text{CuO} \rightarrow \text{Cu}_2\text{O} \rightarrow \text{Cu}^0$. The exchange current density of each process was determined for each sample. At ambient temperature AgCuO$_2$ displays superior rate capabilities for the two highest voltage processes. For all samples, the rate capability of the two lower voltage processes — that of CuO and Cu$_2$O — is always superior to those at higher voltage. This is in part due to the electrode intrinsically doping itself with elemental silver during discharge as part of the second reduction process, which both facilitates excellent electronic contact to the oxide material, as well as mechanically breaks-down the material as a result of Ag$^0$ extrusion from the second discharge process. The electrode compares favourably with commercial electrolytic manganese dioxide but is prone to self-discharge, the kinetics of which are also discussed.

Stemming from the excellent rate capabilities of CuO and Cu$_2$O discharge intermediates of AgCuO$_2$, a library of CuO samples were prepared by conventional (thermal decomposition of Cu(II) salts) and novel (microwave-assisted, hydrothermal etc.) methods, and their electrochemical performance evaluated. A material prepared by the room temperature conversion of Cu(OH)$_2$ precipitated in ethylene glycol solvent (glycol-CuO) possessed superior electrochemical performance, and as such was chosen for fundamental mechanistic studies. This material discharged by a two-step mechanism with a Cu$_2$O intermediate. A material produced from the thermal decomposition of Cu(NO$_3$)$_2$·2.5H$_2$O at 500 °C (nitrate-CuO) displayed a vastly different reduction
mechanism containing only one step, and too was chosen for mechanistic analysis. Amorphous glycol-CuO discharged via two, equivalent charge single electron reduction processes at −0.30 and −0.70 V vs. Hg/HgO, whereas crystalline nitrate-CuO discharged via a single, sharp reduction process at −0.72 V, which integrated to the theoretical capacity of CuO, implying a $2e^-$ reduction to metallic copper. The differences in this behaviour are attributed to a solubility mechanism of discharge, itself derived from indirect evidence of diminishing electrochemical performance in decreasing KOH concentration electrolytes.

The mechanism of the first reduction of glycol-CuO involves the insertion of electrons into the host tenorite CuO structure, before the quick solubilisation of the copper(I) intermediate. The soluble copper(I) intermediate then saturates the electrode, causing a potential depression, which recovers with crystallisation of the soluble material as Cu$_2$O (cuprite). Cu$_2$O then goes on to discharge to Cu$^0$. The soluble intermediate is first hypothesised to account for the drastic decrease in performance with KOH electrolyte concentration (9.0–0.1 M), before being confirmed via its direct electrochemical detection using a novel Pt loop detector electrode. Decreasing the concentration of KOH in the electrolyte decreased the activity of OH$^-$ ions within solution, which contributes to poor kinetics of solubilisation. As this solubilisation step is kinetically poor under low OH$^-$ activity conditions, the electrode discharges via another discharge process equivalent in voltage (once reference electrode activities are taken into consideration) as the nitrate-CuO discharge process mentioned above.

In the case of the reduction of crystalline nitrate-CuO, the highly crystalline nature of the material along with a deceased BET surface area compared to glycol-CuO (191.9 vs. 0.9 m$^2$ g$^{-1}$, respectively) contributes to an overall poor solubilisation for the reduction mechanism, which leads to the different discharge mechanism — one independent of OH$^-$ concentration. The other materials in the CuO library had their performance described in light of the solubilisation mechanism. Those materials with large BET surface areas possessed good electrochemical kinetics on account of their large material|electrolyte interface. This was not the only way to achieve good electrochemical performance however, as materials with large levels of amorphicity also displayed good performance. The impact of both these physico-chemical properties was able to be conveniently analysed in a case study whereby a material with electrochemical performance intermediate to that of two- and one-step materials was compared to other materials with similar levels of crystallinity or size of BET surface
area, but different in the other. The results are consistent with the solubilisation mechanism — other things being equal, a larger BET surface area or lower level of crystallinity will lead to a better electrochemical performance, on account of the increased facilitation of the solubilisation of the soluble copper(I) intermediate.

Due to the solubilisation of CuO in alkaline electrolyte — and the resulting difficulties for a commercial alkaline Zn/CuO cell due to cell gassing — a number of concepts were implemented to attempt to suppress CuO solubilisation or diffusion of the soluble species, Cu(OH)$_4^{2-}$. This included incorporating the material into an alkaline poly(acrylic acid) hydrogel by mechanically grinding CuO material with graphite conductor and electrolyte-softened poly(acrylic acid). Where the hydrogel was included, solubilisation of CuO was suppressed compared to where it was absent, as determined by a novel electrochemical method. However, the electrochemical performance is unacceptably compromised, so no further investigation was performed.

Whilst no separator technology was tested to limit Cu(OH)$_4^{2-}$ movement, the ramifications of a successful separator were investigated. If any separator technology were uncovered which was impermeable to Cu(OH)$_4^{2-}$, then an alkaline Zn/CuO cell would offer a potential solution to the cell gassing problem. The electrochemical performance of Cu(OH)$_4^{2-}$-saturated 9.0 M KOH was also investigated. This test was done to mimic conditions a commercial cell would encounter when its manufacture and shelf life are considered, where the electrolyte in the cathode compartment would become saturated in copper. The testing indicates that despite the solubilisation mechanism of CuO discharge, performance in Cu(OH)$_4^{2-}$-saturate 9.0 M electrolyte is not greatly compromised.

A series of mixed-metal LiFe$_{1-y}$Mn$_y$PO$_4$/C olivine composites were prepared via a simple single-step non-aqueous sol-gel technique. The materials were characterised by X-ray diffraction to be of good phase purity, and the unit cell parameters followed Vegard’s law with the increased concentration of manganese in the material. Materials prepared where manganese was present took on a novel cross-like morphology, with particle sizes ranging from 1.5−8.0 µm, depending on agglomeration.

The materials were cycled in both conventional 1 M LiPF$_6$ in 1:1 ethylene carbonate/dimethyl carbonate and 0.5 mol kg$^{-1}$ lithium bis(trifluoromethane-sulfonyl)imide salt in N-methyl-N-propyl-pyrrolidinium bis(fluorosulfonyl)imide ionic liquid electrolyte. Where the ionic liquid was used, superior cycling performance was observed. This may be due to the decreased electrochemical decomposition of
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