

# **ELECTROCHEMICAL SYNTHESIS OF INORGANIC MATERIALS AND THEIR APPLICATION AS ANODES FOR Li-ION BATTERIES**

## **A Synopsis**

The major concern of materials chemistry is to synthesize materials with a predetermined structure, morphology and orientation. The conventional ceramic method results in the formation of thermodynamically stable phases. Many low temperature methods have been introduced in order to synthesize the desired materials in novel structures, controlled morphology and growth direction. Among these, electrosynthesis is an ambient temperature technique. Since the reaction takes place within the electric double layer close to the electrode, the products are deposited as thin and thick films or coatings with good adherence to the substrate. Further, the potential gradient at the electric double layer is of the order  $10^5 \text{ V cm}^{-1}$ . Under this gradient the reactant moieties are highly polarized and thereby product obtained could potentially be different from that obtained by chemical synthesis. Thus phase selection, morphology and crystal growth can be kinetically and thermodynamically controlled by the use of electrochemistry.

Lithium ion batteries are presently the prime energy source for portable electronic devices. They have a long life span, high energy density and are environmentally safe. With the exception of  $\text{LiFePO}_4$  and anatase  $\text{TiO}_2$ , lithium ion batteries do not show any memory effects. Carbonaceous materials such as graphite, cokes and graphitized carbons are commercially used as anode materials in Li-ion batteries. Recently *3d* transition metal oxides have been extensively studied as anode materials because of their high specific capacity, high volumetric energy density and safety. The mechanism of action of metal oxide anodes differs from that of carbonaceous materials. In place of the well known reversible intercalation mechanism, metal oxide anodes involve a conversion process in

which  $\text{Li}_2\text{O}$  forms during charge and decomposes during discharge along with the concomitant reversible reduction of the transition metal oxide.

In general, preparation of metal oxide anodes for Li-ion batteries involves a two-step process.

1. Synthesis of the required metal oxide at high temperature.
2. Fabrication of the electrode by smearing or spin coating of metal oxides slurries on a suitable substrate along with carbon powder as conducting additive and a polymer binder.

In this thesis, we combine the one-step electrosynthesis of films and coatings of inorganic materials with their application as anodes for lithium ion batteries. This thesis consists of eight chapters. A brief description of each chapter is given below.

### **Chapter 1: Introduction**

In the first chapter, special emphasis is given to contemporary concerns in materials chemistry. A detailed discussion on employing electrochemistry to address these concerns is presented. A brief description on electrodeposition of transition metal oxides and their application in Li-ion batteries is given.

### **Chapter 2: Electrodeposition of crystalline and amorphous $\text{CaCO}_3$ on stainless steel substrates in the presence of complexing agents**

Highly crystalline calcite  $\text{CaCO}_3$  was deposited by cathodic reduction of a calcium bicarbonate bath in the presence of different aminocarboxylic acids as complexing agents. In presence of 5 mole% Sr, the coatings obtained were X-ray amorphous. In the absence of Sr, the powder X-ray diffraction (PXRD) patterns of the as-deposited coatings obtained from the bath with  $[\text{DTPA}]/[\text{Ca}^{2+}]$  ratio  $< 1$ , (DTPA: diethylenetriaminepentaacetic acid)

exhibit all the reflections corresponding to calcite  $\text{CaCO}_3$ . At  $[\text{DTPA}]/[\text{Ca}^{2+}] \geq 1$ , the PXRD pattern shows only the 104 reflection, which is indicative of a 104 out of plane orientation. Mineral calcite generally shows rhomboidal morphology, which was observed when EDTA (ethylenediaminetetraacetic acid) was used as a complexing agent. In presence of DTPA, platelet morphology was observed. Amorphous  $\text{CaCO}_3$  coatings show floral and dumbbell morphologies

### **Chapter 3: Electrodeposition of $\text{MCrO}_3$ (M = La, Dy, Nd, Pr, Gd and Y) perovskite oxide coatings on stainless steel substrates**

One of the significant challenges of the effective use of functional oxide materials in device applications is to obtain them in the form of thin films or thick coatings. In this work, we show cathodic electrodeposition technique as a cost effective method for fabrication of perovskite chromite coatings. Amorphous precursor hydroxide coatings of M (M = La, Pr, Nd, Gd, Dy, Y) and Cr were co-deposited on stainless steel electrode by cathodic electrodeposition from a nitrate bath. These precursor coatings were further heat treated to obtain  $\text{MCrO}_3$  perovskite oxide coatings. Heat treatment of La-Cr hydroxide precursor coatings at 600 °C and 800 °C resulted in coatings of  $\text{La}_2\text{CrO}_6$  and  $\text{LaCrO}_3$  phases respectively. The other M-Cr hydroxides on heating at 800 °C for 2 hours formed respective single phase  $\text{MCrO}_3$  perovskite coatings. Interestingly, the SEM images of heat treated perovskite coatings show different morphologies with varying M in  $\text{MCrO}_3$  (M = La, Pr, Nd, Gd, Dy and Y).

### **Chapter 4: Effect of orientation on the reversible discharge capacity of electrodeposited $\text{Cu}_2\text{O}$ coatings as lithium-ion battery anodes**

Electrodeposited  $\text{Cu}_2\text{O}$  coatings with 111 out-of-plane orientation were found to have the lowest reversible discharge capacity as anodes for Li-ion cells. This is attributed to the low surface energy and the consequent high thermodynamic stability of the 111 crystal

face of  $\text{Cu}_2\text{O}$ . In contrast the 200 oriented coating has a higher reversible discharge capacity, owing to its polar nature and high surface energy. The highest reversible discharge capacity was observed for unoriented coatings, emphasizing the critical role played by grain boundaries in the conversion electrodes. The morphology of crystallites in the electrodes recovered after cycling is different in the three cases suggesting that the nature of reversible chemical conversion is guided by physical attributes of the precursor  $\text{Cu}_2\text{O}$  crystallites.

### **Chapter 5: Electronic structure calculation for Lithium insertion in $\text{Cu}_2\text{O}$**

The successful use of metal oxides as conversion anodes in Li-ion batteries invokes the formation and subsequent reductive decomposition of  $\text{Li}_2\text{O}$ . Given the standard reduction potential of  $\text{Li}/\text{Li}^+$  couple, the reduction of  $\text{Li}_2\text{O}$  to Li is a thermodynamic challenge. There is as yet no evidence either by experiment or theory that such a process is feasible. In this chapter we investigate the interaction of  $\text{Li}^+$  ions with a matrix of  $\text{Cu}_2\text{O}$  computationally using the first principles based DFT + U methodology. This study indicates that alloying of Cu and Li takes place more readily than  $\text{Li}_2\text{O}$  formation in the early part of the charge cycle. We surmise that capacity fading observed in oxide conversion anodes is likely the result of irreversible accumulation of  $\text{Li}_2\text{O}$ , and reversible alloying plays a greater role in the charge-discharge process than has been generally acknowledged.

### **Chapter 6: Electrochemical impedance studies of capacity fading of electrodeposited ZnO conversion anodes in Li-ion battery**

Electrodeposited ZnO coatings suffer severe capacity fading when used as conversion anodes in sealed Li cells. Capacity fading is attributed to (i) the large charge transfer resistance,  $R_{\text{ct}}$  (300 – 700  $\Omega$ ) and (ii) the low  $\text{Li}^+$  ion diffusion coefficient,  $D_{\text{Li}^+}$  ( $10^{-15}$  –  $10^{-13}$   $\text{cm}^2 \text{ s}^{-1}$ ). The measured value of  $R_{\text{ct}}$  is nearly ten times higher and  $D_{\text{Li}^+}$  ten to

hundred times lower than the corresponding values for  $\text{Cu}_2\text{O}$ , which delivers a stable reversible capacity.

## **Chapter 7: Electrochemical behaviour of NiO conversion anodes in Li-ion batteries:**

### **Effect of crystallite size and nonstoichiometry**

Conversion anodes comprising non-stoichiometric black NiO suffers severe capacity fading in Li-ion batteries. We attribute this capacity fading to (i) its small crystallite size (~8 nm), and (ii) high charge transfer resistance ( $R_{ct}$ ). In contrast the stoichiometric green NiO anodes deliver a stable capacity of  $280 \text{ mAh g}^{-1}$  over 50 charge-discharge cycles. The comparatively higher capacity of green NiO can be explained from its (i) negligible  $R_{ct}$  values, and (ii) large crystallite size (~104 nm).

## **Chapter 8: Conclusions**

In this chapter, the conclusions of the thesis have been summarized. The inherent limitations of this thesis and the future scope of research regarding the electrodeposition of other inorganic materials and their application as electrodes for Li-ion batteries are discussed.