

# NANOSTRUCTURED METAL OXIDES FOR HIGH-POWER BATTERIES

Final Report

JPL Task 1012

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## A. OBJECTIVES

Lithium ion rechargeable batteries have started replacing the conventional aqueous rechargeable battery systems in NASA's space missions. Despite their manifold enhancements in specific energy and energy density over the aqueous systems, and their superiority in low-temperature operation, self-discharge and energy efficiency, they are ranked behind the alkaline systems, such as Ni-Cd, Ni-H<sub>2</sub> and Ag-Zn from a high-power standpoint. The relatively low power densities of lithium ion are attributed to slow lithium intercalation kinetics at both positive and negative electrodes. Electrodes with nanostructured features, e.g., nanoparticles, nanofibers, nanowires, etc. are expected to have much larger effective surface and interfacial areas, thus facilitating faster rates of Li intercalation and higher power densities. The objectives of the proposed work are to synthesize nanostructured metal oxides for cathode applications in lithium-ion rechargeable batteries, using novel template and sol-gel or electrolytic synthetic techniques. Such nanostructured morphologies, e.g., nanowires, will have high aspect ratios of 10-100 and thus enhance the power densities and high-rate-energy densities of the devices by 1-2 orders of magnitude, compared to the state-of-the-art devices, while preserving comparable footprints. Apart from the batteries, these nanocathodes will benefit several other electrochemical devices, e.g., electrochromic devices and microsensors.

## B. PROGRESS AND RESULTS

High surface electrodes, e.g., nanowires with high aspect ratios, are possible cathode morphologies for high-power-density applications, as demonstrated with tin oxides and vanadium oxide cathodes.<sup>1-3</sup> These cathodes were fabricated by sol-gel deposition into nano-channels in porous alumina templates.<sup>2</sup> We have followed a slightly different approach to synthesize nanowires of the state-of-practice lithium-ion cathodes, i.e., lithiated cobalt oxide and lithiated nickel oxides, as described below.

We used alumina template, synthesized in-house with a typical diameter of 20 nm (Fig. 1). The porosity and pore diameter of the alumina template can, however, be varied by changing the anodizing conditions of aluminum sheet. This in-house capability allows for direct on-silicon fabrication, of interest for micro-power applications. A current collector, either Au or Pt, is deposited on one end of the porous alumina, and from the open end, transition metals -- either cobalt or nickel -- are deposited electrochemically. Nanowires of either cobalt or nickel, with high aspect ratios were thus formed. The alumina template is then digested, leaving nanowires of either cobalt or nickel, as illustrated in Fig. 2.

Preliminary attempts to lithiate these nanometallic wires, to form lithium cobalt or nickel oxide nanowires, haven't been successful. We attempted lithiation of these nanowires both in the aqueous and non-aqueous media, but were not successful. The electrochemical activity of these cobalt and nickel oxide nanowires is thus comparable to the bulk material. Further studies are warranted to resolve this.

Meanwhile, using a similar approach, we have been able to successfully fabricate freestanding arrays of amorphous manganese oxide nanowires from electrolytic sulfate baths under both acidic and alkaline conditions (Fig. 3). The stoichiometry (verified via XPS characterization) of the nanowires could be tailored from  $\text{Mn}_2\text{O}_3$  –  $\text{Mn}_3\text{O}_4$  –  $\text{MnO}_2$  by adjusting deposition potential and bath chemistry. After characterizing the amorphous manganese oxide nanowires by SEM, EDS and Synchrotron crystallography, these nanowire arrays were assembled with a Li counter electrode and non-aqueous electrolyte to form secondary batteries. These cells were capable of multiple charge/discharge cycles, with a cathode specific capacity of  $\sim 300$  mA-hr/g. The electrodes, fabricated without any conductive diluent, could support current of  $0.1$  mA/cm<sup>2</sup> (Fig. 4) and showed good reversibility (Fig. 5) in laboratory test cells against Li in Li ion battery electrolyte solutions.

Although some of these compositions of manganese oxides are the most desirable for battery and supercapacitor applications, the other stoichiometries may be of interest for high-surface-area catalysis applications.

### **C. SIGNIFICANCE OF RESULTS**

We have been able to successfully synthesize various transition metal oxide cathodes, e.g., cobalt, nickel and manganese oxides, in the form of nanowires with typical diameters of 20 nm. In addition, arrays of free-standing manganese oxide nanowires with comparable electrochemical activity have been synthesized. Combining such nanowire cathodes with a lithium anode in a suitable device, i.e., either a polymer electrolyte cast from solution, or a solid electrolyte sputter- or vapor-deposited, will result in a thin film battery with severalfold increase in the power densities (which is one deterrent factor for polymer electrolyte) or thin film or microbatteries. Increased power densities, achieved without increasing the footprint, is a very attractive option from a spacecraft standpoint. Finally, the above approach to combine template synthesis with electrochemical deposition for nano-morphologies will be useful not only for batteries, but also in sensors and catalysis.

### **D. FINANCIAL STATUS**

The total funding for this task was \$115,000, all of which has been expended.

### **E. PERSONNEL**

No other personnel were involved.

## F. PUBLICATIONS

- 1) A paper entitled “Synthesis of LiCoO<sub>2</sub> Nanowire Arrays from Co Electrodeposits” and authored by W. C. West, N. V. Myung, J. F. Whitacre, and B. V. Ratnakumar, was presented at the “Nanophase Materials for Batteries and Fuel cells” symposium at the American Electrochem. Soc. Spring Meeting, in Philadelphia on May 2002.
- 2) An NTR was submitted describing processes to fabricate nanostructured electrode materials: “Direct Electrolytic Deposition of Manganese Oxide Nanowires for High Power Battery and Capacitor Electrodes”, W. C. West, N. Myung, J. Whitacre, B. V. Ratnakumar, *NASA New Technology Report # 30655*, (2002).
- 3) The group was solicited to present an invited paper describing nanostructured materials for batteries at the NanoEnergy Conference in Miami, FL in Dec. 2002. Will West will present: “Freestanding Arrays of Nanowire Materials for High Rate Capability Battery Electrodes”.
- 4) A paper, entitled “Electrodeposited Amorphous Manganese Oxide Nanowire Arrays for High Energy and Power Density Electrodes”, by W. C. West, N. V. Myung, J. F. Whitacre, and B. V. Ratnakumar was accepted for publication in the *Journal of Power Sources*.

## G. REFERENCES

1. N. Li, C. R. Martin, and B. Scrosati, *Electrochem. Solid State Lett.*, 3, 316 (2000).
2. N. Li, C.R. Martin, and B. Scrosati, *J. Power Sources*, 97-98, 240 (2001).
3. C. J. Patrissi, and C. R. Martin, *J. Electrochem. Soc.*, 146, 3176 (1999).

## H. FIGURES

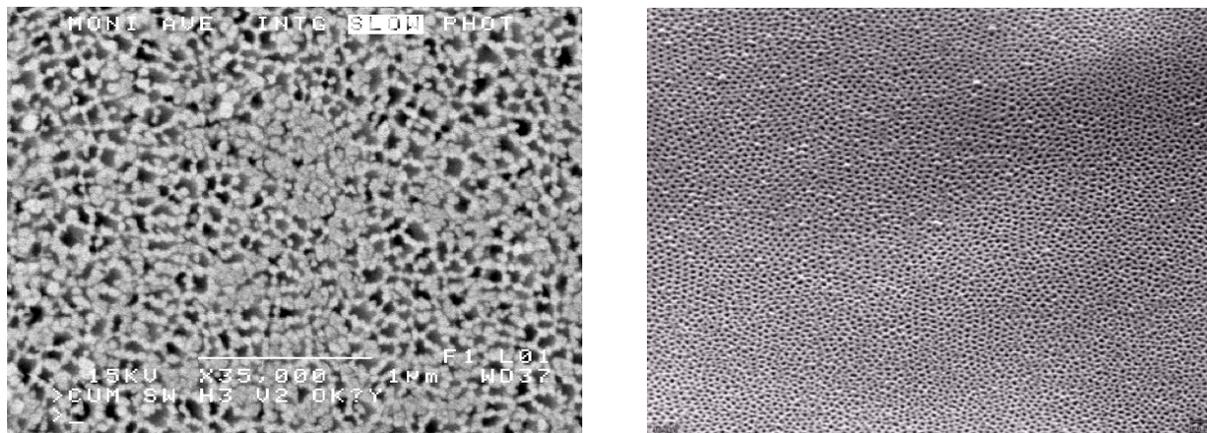


Fig. 1 Whatman Anodisc (100 nm pores) JPL synthesized alumina template (20 nm pores)

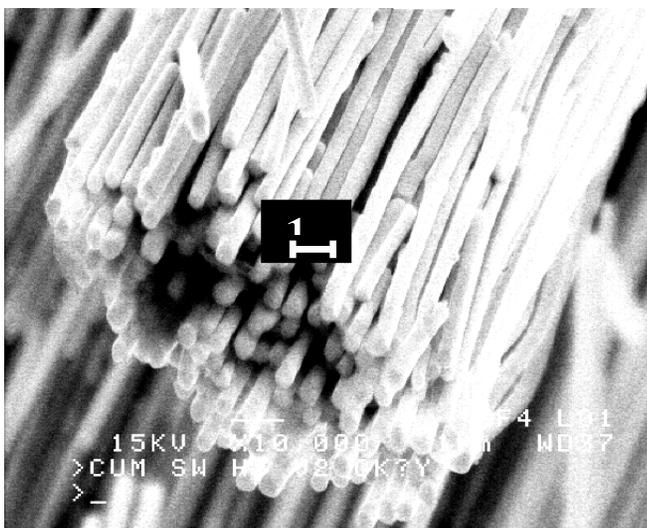


Fig. 2. Nanowires of Co(Ni) for fabrication of nanostructured  $\text{LiCoO}_2$ .

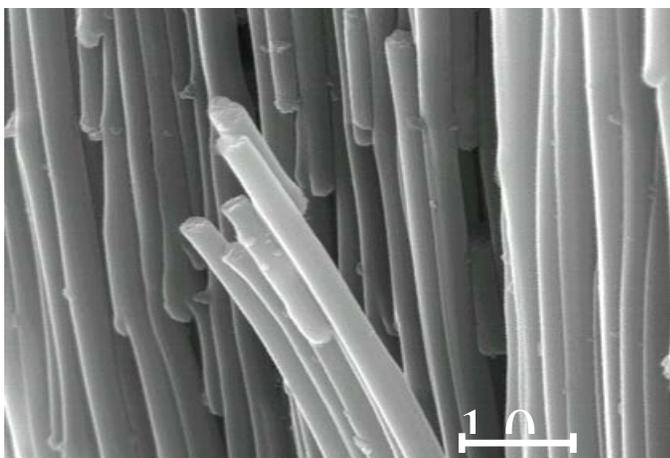


Fig. 3. Nanowires of Manganese oxides from sulfate bath

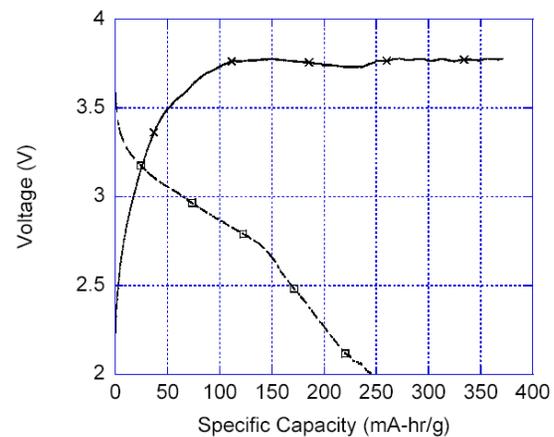


Fig. 4: Charge-discharge curves of Nanowire manganese oxide wires against Li electrode in 1M  $\text{LiPF}_6/\text{EC}:\text{DEC}:\text{DMC}$  solution.

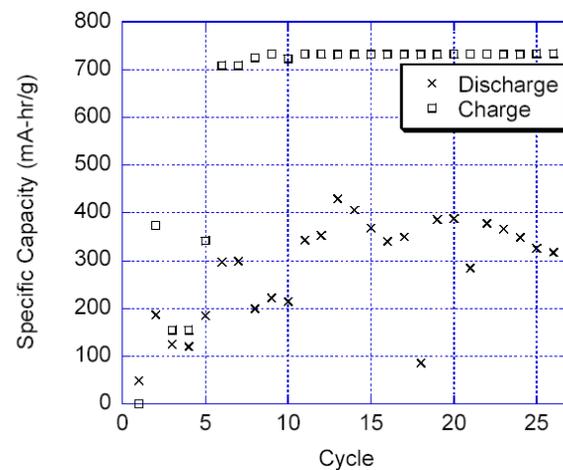


Fig. 5: Capacity of Nanowire manganese oxide wires against Li in 1M  $\text{LiPF}_6/\text{EC}:\text{DEC}:\text{DMC}$  during electrochemical cycling.