

# Synthesis of LiCoO<sub>2</sub> Nanowire Arrays from Co Electrodeposits

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The power density of a Li-ion cell is dictated, at the fundamental level, by the electrochemical kinetics (of charge transfer) at the electrode/electrolyte interface and the kinetics of solid-state diffusion of lithium ions in the host electrodes. Thus, the rate capability of battery cathodes is highly dependent on the grain size, texture, and morphology of the electrode materials. The ability to engineer an ordered, high surface area structure of electrochemically active materials on the nanoscale can yield enhanced charge/discharge characteristics. For example, other groups have demonstrated that high surface area nanowire arrays of V<sub>2</sub>O<sub>5</sub> have improvements in rate capability of roughly a factor of five compared with thin film control electrodes [1]. We have recently demonstrated the ability to fabricate freestanding nanowires of the more commonly used Li-ion cathode, LiCoO<sub>2</sub>, using templated electroplating and anodic oxidation of the metallic nanowires.

First, nanoporous alumina membranes (Whatman Anodisc 13) with nominal pore diameters of 100 nm were coated on one side with sputter-deposited Au films. The membranes were then attached to C tape and immersed in a Co plating bath. Nanostructured Co electrodes were electrodeposited in the alumina template from a cobalt sulphate bath (0.2 M CoSO<sub>4</sub> + 0.7 M Na<sub>2</sub>SO<sub>4</sub> + 0.4 M H<sub>3</sub>BO<sub>3</sub> + 0.0075 M Saccharin, pH = 3) at 10 mA/cm<sup>2</sup>. The solution pH was adjusted with HCl, H<sub>2</sub>SO<sub>4</sub>, NaOH or NH<sub>4</sub>OH. Concentrated KOH or NaOH (20 v/v %) was used to remove the anodized alumina template, leaving free standing Co nanowires (Fig. 1.)

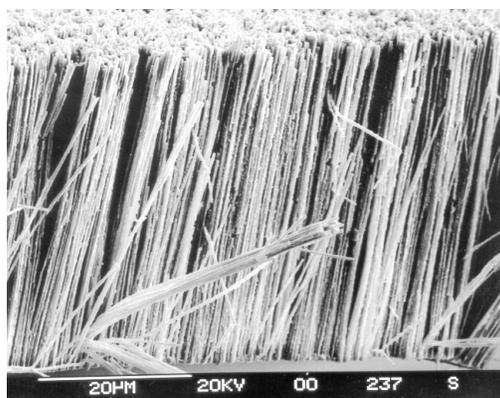


Fig. 1. Free standing Co nanowires.

The conversion of Co to LiCoO<sub>2</sub> can be accomplished by either hydrothermal treatment [2] or anodic oxidation of an aqueous LiOH solution. The freestanding Co nanowires on C tape were immersed in a 4 M LiOH bath and anodically oxidized at a current density of 1 mA/cm<sup>2</sup> for approximately 20 hours. The lithiated and oxidized Co nanowires were subsequently annealed at 800°C for four hours to achieve the layered rhombohedral LiCoO<sub>2</sub> structure (Fig. 2), as verified via x-ray diffraction (Fig. 3).

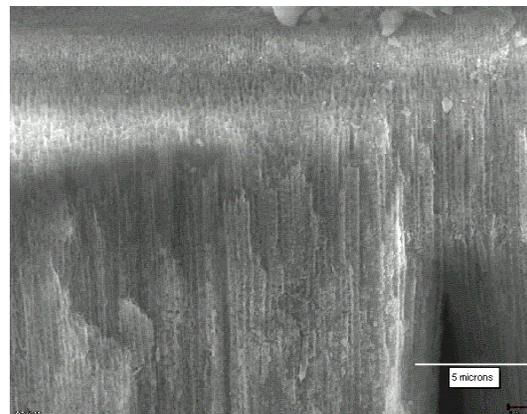


Fig. 2. Array of LiCoO<sub>2</sub> nanowires.

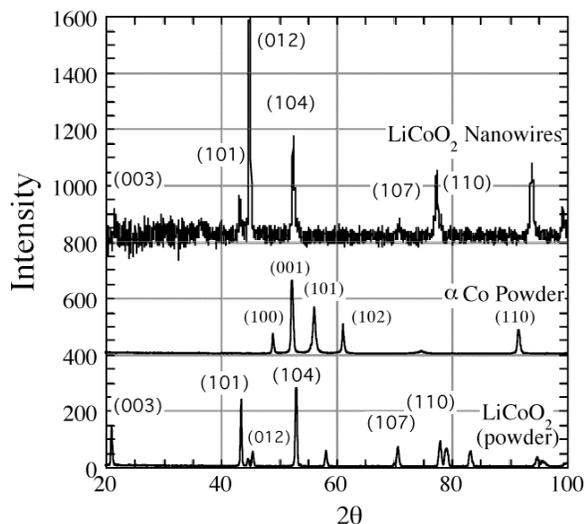


Fig. 3. X-ray diffraction pattern for LiCoO<sub>2</sub> nanowires, compared with Co and powdered LiCoO<sub>2</sub> standards. The incident radiation was Co K $\alpha$  ( $\lambda = 1.79 \text{ \AA}$ ).

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## References

- [1] C. J. Patrissi and C. R. Martin, *J. Electrochem. Soc.*, **146**, 3176 (1999); C. J. Patrissi and C. R. Martin, *J. Electrochem. Soc.*, **148**, A1247 (2001).
- [2] K.-S. Han, S.-W. Song, T. Watanabe, and M. Yoshimura, *Electrochem. Solid State Lett.* **2**, 63 (1999); K.-S. Han, S.-W. Song, H. Fujita, and M. Yoshimura, *Solid State Ionics*, **135**, 273 (2000).