

As-Deposited Thin-Film Battery Cathode Layers

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At present, the best thin film battery cathode layers require either an elevated temperature growth environment¹ or a high-temperature (~700 °C) post-deposition anneal step to encourage the formation of the crystalline microstructure that is associated with dramatically increased battery capacity.² These steps are not necessarily compatible with SOI back-end processing methodology, posing a problem for any application that calls for the direct integration of the battery into a micro-circuit. The goal of this work is to create, via the manipulation of growth parameters and sputter target composition, Li-based cathode layers grown at room temperature that perform relatively well in a thin film battery setting *as deposited*.

To this end, a systematic study of rf magnetron sputtered LiCoO_2 and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films has been undertaken in an attempt to relate growth conditions to film composition, microstructure, and electrochemical performance. Films were grown to a thickness of ~0.3 μm in sputter gases (pressures from 2 to 20 mTorr) consisting of Ar and O_2 mixed at various ratios. Typical cathode forward power was 100 W, while the substrates could be biased using a DC or an rf power source. Film structure and texturing was subsequently examined using x-ray diffraction and TEM, while composition was determined using a combination RBS, ICP-MS, EELS, and PIGE. The electrochemical performance of the layers (both in liquid electrolyte 1/2 cells and thin-film batteries) was studied using cyclic voltometry, and impedance spectroscopy.

Results show that both target composition and substrate bias can dramatically affect film microstructure and performance. For example, figure 1 shows cycling results from liquid

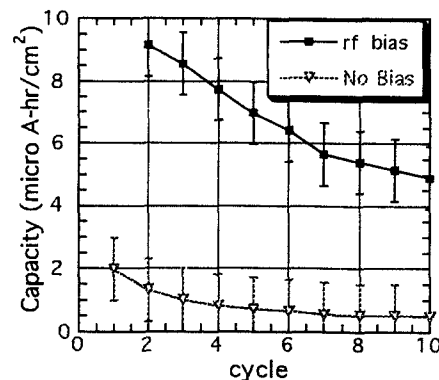


Figure 1: Effect of substrate bias on layer capacity.

electrolyte 1/2 cells made from films sputtered from LiCoO_2 targets in a 9/1 Ar/ O_2 gas mix with and without rf substrate bias. The film grown with bias has a significantly higher capacity than the film grown with no bias. This effect has

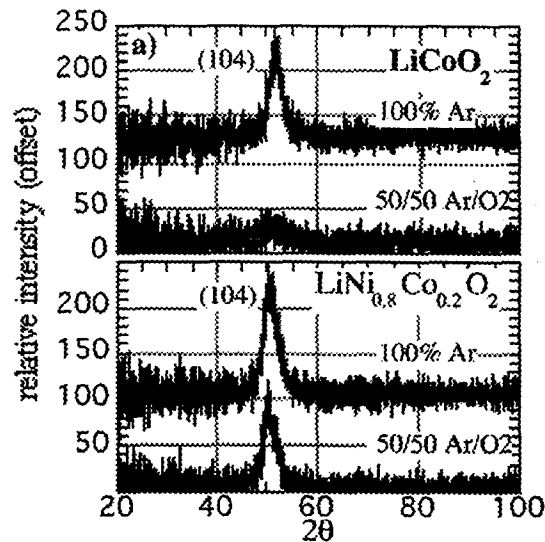


Figure 2: XRD patterns of cathode layers.

been related to both film composition and microstructure.

Another relevant finding concerns the X-ray data (figure 2) collected from LiCoO_2 and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films deposited in pure Ar and a 50/50 Ar/ O_2 mix.

The diffraction patterns indicate that, contrary to results published elsewhere^{3,4}, it is possible to grow crystalline (grain size ~ 10nm) LiCoO_2 and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films with a strong (104) out of plane texture.

The texturing in the LiCoO_2 film is strongly dependent upon the O_2 content of the sputter gas, whereas the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films maintained much of their texture despite the presence of O_2 .

These findings are relevant since increased cathode capacity has been found to be related to both the degree of (104) out of plane texture⁵ as well as sputter gas O_2 content.⁶

All findings will be discussed in the context of previous theoretical and experimental findings that address the structure-composition-performance relationship for thin-film solid state electrodes.

¹ N.J. Dudney et al., *J. Electrochem. Soc.* **146**(7) 2455-2464 (1999)

² Bates et al. *J. Power Sources* **54**, 58-62 (1995)

³ H. Benqlilou-Moudden et al., *Thin Solid Films*, **333**, 16-19 (1998).

⁴ P. Fragnaud et al., *J. Power Sources* **63** 187-191 (1996)

⁵ F.X. Hart et al., *J. Appl. Phys.* **83**(12) 7560 (1998)

⁶ W.C. West et al, Fall 1999 ECS proc. (in press)