

## Thin Film Lithium Batteries Prepared by Spray Pyrolysis

P. Fragnaud and D.M. Schleich

Laboratoire de Genie Des Materiaux , ISITEM  
La Chanterie, 44087 Nantes Cedex 03, France

**Abstract.** We have prepared thin film cathode materials and thin film electrolytes at temperatures ranging from 400°C to 600°C by a spray pyrolysis technique. The sols used to prepare the films are made from simple inorganic salts and non toxic, inexpensive diols. The sols can be sprayed in an air atmosphere to prepare films of the desired crystalline materials.

### 1. Introduction

Thin film techniques are extremely important in a wide range of solid state technologies. The thin film, all solid state, secondary battery is of interest for certain specialized applications. The concept of a thin film solid state battery is not new and was demonstrated more than 10 years ago [1,2]; however, there is renewed interest due to the special characteristics of such a device [3].

In general the thin film solid state battery is based on an intercalation cell. The major advantage of this all solid state cell is the large number of recharges that are available. Cell cycles in excess of 10,000 have been observed in simple Li/TiS<sub>2</sub> cells [4]. This advantage occurs since there are no deleterious reactions between liquid electrolytes and the active electrodes. This lack of electrode/electrolyte interaction is perhaps even more important as one looks at cells capable of delivering more than 4.0 volts. In addition, since ionic mobility within the insertion electrodes can limit the rate of discharge within the cell, reducing the thickness of the components can limit the polarization occurring during high current densities.

The published efforts on the preparation of thin film cells have been limited to physical vapor deposition techniques (sputtering, evaporation, laser ablation, molecular beam epitaxy etc.), and although these techniques are widely used in the semiconducting industry, we felt that a simple chemical process may have certain advantages. We have explored the deposition of active cathodes and lithium electrolytes by a simple, low cost spray pyrolysis technique. This

process has allowed us to prepare a wide range of active cathodes (LiCoO<sub>2</sub>, LiCo<sub>1-x</sub>Ni<sub>x</sub>O<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub> and V<sub>2</sub>O<sub>5</sub>) as well as the lithium ion conductor  $.4\text{Li}_3\text{VO}_4/.6\text{Li}_4\text{GeO}_4$  at temperatures as low as 450 °C. The particular cathode materials were chosen since they possess excellent energy characteristics and they are all stable in air. The electrolyte was chosen because of its very good electrical conductivity ( $4 \times 10^{-5}$  at 18°C) [4], its broad electrochemical window and its high temperature capabilities [5].

### 2. Experimental Procedures

Thin films of all the materials were obtained by spraying a sol onto a heated substrate. The spraying was accomplished with a simple air brush (Paasche F#1), in air and the substrate was heated resistively. The concentration of the sol was varied to modify the morphology of the film.

**2.1 Cathode Sols.** Sols of the desired lithiated metal oxide were prepared by reacting the simple hydrated transition metal nitrate and lithium nitrate with propylene or ethylene glycol (all compounds were used as obtained from Aldrich Chemical Co.). Sols of vanadium oxide were obtained by reacting either VCl<sub>4</sub> or VOCl<sub>3</sub> with the desired diol. The solutions (0.01 - 0.4 M) obtained by dissolving the transition metal compounds were heated under flowing nitrogen at temperatures ranging from 90°C to 150°C for 1-5 hours. All reactions were performed in air except those involving the hygroscopic vanadium compounds that must be performed in a dry box (warning the vanadium reaction is violent!).

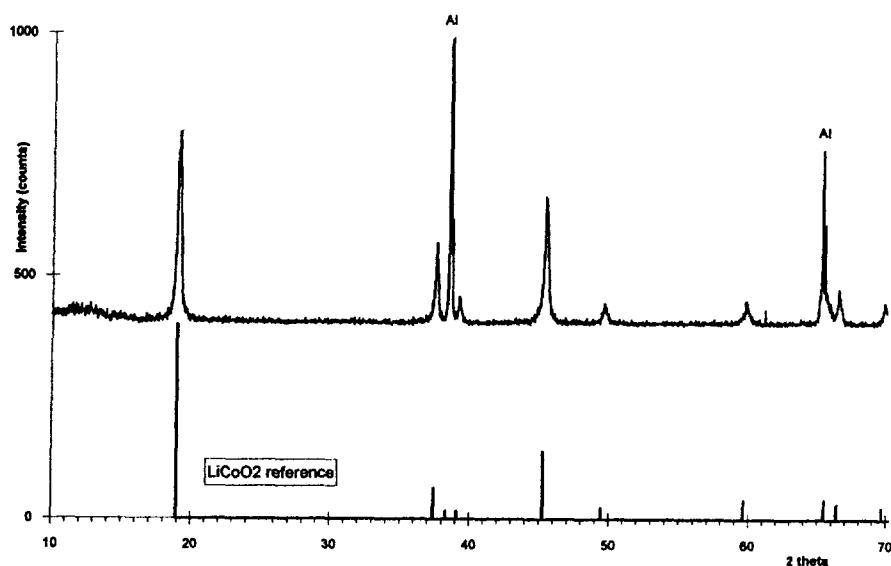


Fig. 1. X-ray powder diffraction pattern of  $\text{LiCoO}_2$  thin film on aluminum foil substrate (500°C anneal for 18 hours after spray onto 450°C substrate)

**2.2 Electrolyte Sol.** The sol was prepared by adding  $\text{GeCl}_4$  to propylene or ethylene glycol. This germanium containing sol is kept in a dry environment. A sol containing lithium and vanadium is prepared by adding an active vanadium compound ( $\text{VCl}_4$  or  $\text{VOCl}_3$ ) and lithium nitrate to propylene or ethylene glycol. This sol is then heated to dissolve the polymeric or oligomeric species formed. The germanium sol is now added to this vanadium/lithium sol and subsequently heated.

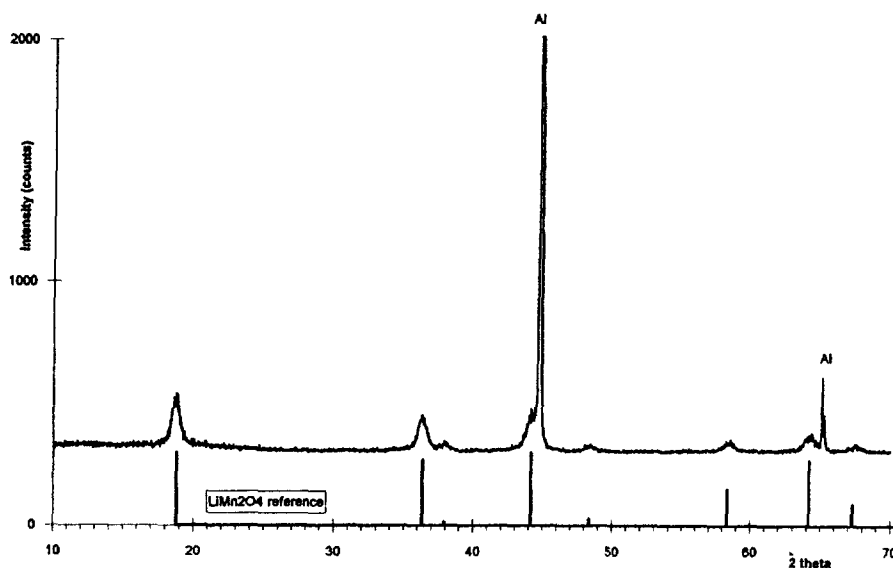


Fig. 2. X-ray powder diffraction pattern of  $\text{LiMn}_2\text{O}_4$  thin film on aluminum foil substrate (spray onto 450°C substrate, no anneal)

### 2.3 Electrolyte Sol Treatment.

In order to obtain the desired compound it was necessary to remove all chloride from the sol. This was accomplished by titration with a silver nitrate solution in a glycol solvent. After the chloride was removed by formation of an insoluble silver chloride precipitate, the silver ion concentration readily increased and was detected by an ion selective electrode. The silver chloride precipitate was removed by filtration after heating of the sol to increase particle size.

We verified the polycrystalline phases present by X-ray powder diffraction (Phillips XRD 3100,  $\text{CuK}\alpha$  radiation, reference patterns from JCPDS

files) and determined the characteristics of the precursors by thermal gravimetric analysis (TGA), differential scanning calorimetry (Perkin Elmer DSC-4) and Fourier transform infra red spectroscopy (Perkin Elmer 16 PC FT-IR).

## 3. Results and Discussion

**3.1 Cathode Films.** The sols of  $\text{LiCoO}_2$ ,  $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$ , and  $\text{LiMn}_2\text{O}_4$  were sprayed directly onto heated substrates (aluminum foil, gold foil, pyrex and silica). The temperature of the heating plate used to heat these substrates was varied from 200°C to 550°C. At the lowest temperature the polymeric precursor is not entirely decomposed, whereas at the higher temperatures X-ray powder diffraction indicates that the desired phase is prepared without additional annealing. Figs. 1 and 2 show the X-ray powder diffraction spectra of  $\text{LiCoO}_2$  and  $\text{LiMn}_2\text{O}_4$  films respectively on aluminum foil substrates. These films were sprayed onto substrates at 450°C. The  $\text{LiCoO}_2$

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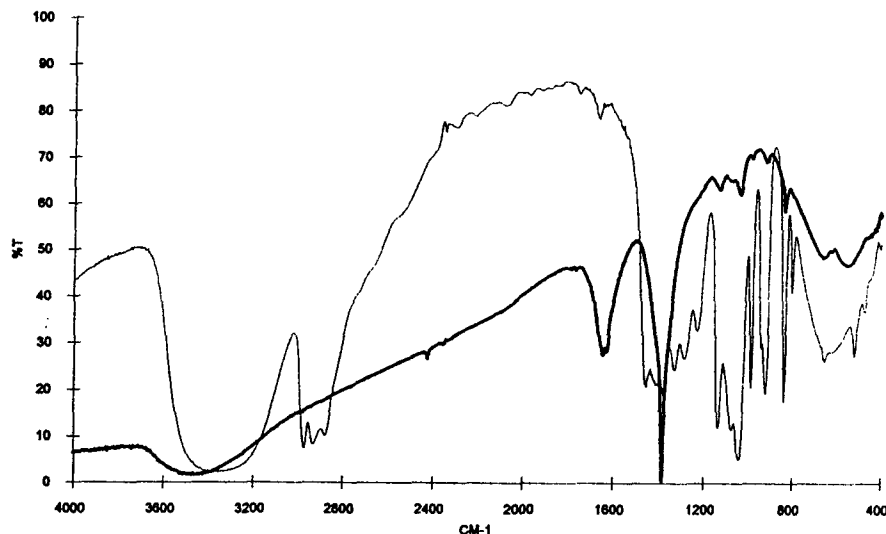


Fig. 3. FTIR spectra of vacuum dried LiCoO<sub>2</sub> precursor (heavy line), and propylene glycol reagent (light line)

film was subsequently annealed at 500°C for 18 hours to increase crystallite size and thus one can observe the narrowing of the diffraction peak width. In all cases, independent of the substrate temperature during spraying, the desired phase was prepared as long as the film was subjected to a temperature greater than 400°C. Further annealing at either higher temperature or for longer times resulted in larger crystallite sizes. The substrate temperature during

spraying substantially modifies the morphology and adhesion of the films. Spraying at low substrate temperatures results in porous films with poor mechanical strength, whereas high temperature (i.e., > 400°C) spraying results in dense, tough films with good adhesion to

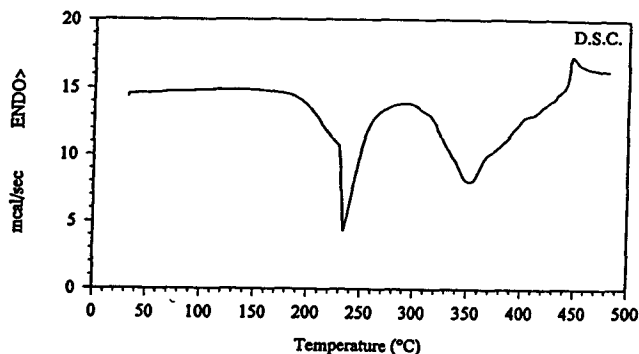


Fig. 4. Differential scanning calorimetry data of vacuum dried LiCoO<sub>2</sub> sol in an air atmosphere (5.9 mg, 10 deg/min)

aluminum foil.

FTIR spectra were performed on the sols after vacuum elimination of excess diol, serving as solvent, at 80°C. The resulting powders were mixed with KBr (1% by weight) and pressed into standard 1 cm pellets. The spectrum of a LiCoO<sub>2</sub> precursor is shown in Fig. 3. The most striking features are the strong carbonyl peak at 1640 cm<sup>-1</sup>, and the loss in the CH peak at 2860-2990 cm<sup>-1</sup> present in the original glycol.

Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed in an air atmosphere on

the vacuum dried sols. Typical results are shown in Figs. 4 and 5. An initial decomposition is observed at approximately 200-220°C, followed by a second decomposition at 290-340°C. Both of these reactions are highly exothermic (340 cal/gram and 320 cal/gram respectively). We also performed a TGA under nitrogen on a larger sample size (70 mg rather than the usual loading of 10 mg of LiCoO<sub>2</sub> precursor). Under these conditions an extremely rapid one step decomposition occurs (see Fig. 6). X-ray diffraction of the sample after the TGA run verified the transformation to single phase

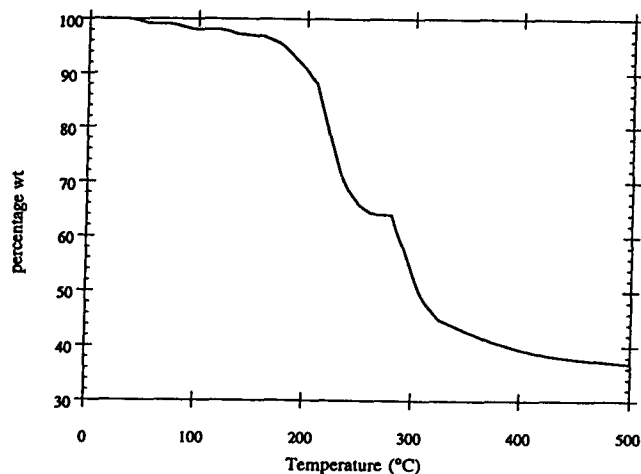


Fig. 5. Thermal gravimetric analysis of vacuum dried LiCoO<sub>2</sub> sol in an air atmosphere (13 mg, 10 deg/min)

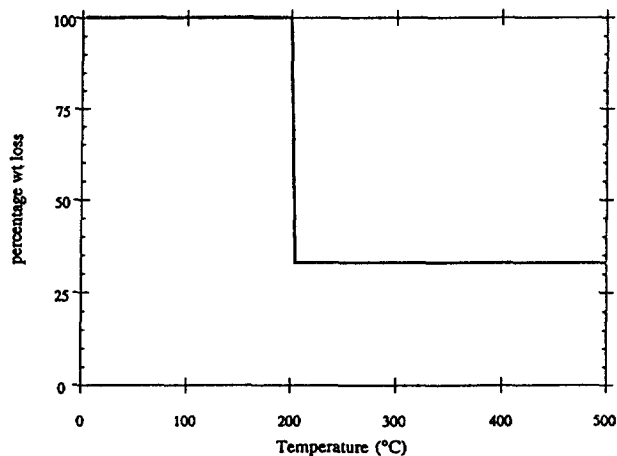


Fig. 6. Thermal gravimetric analysis data of vacuum dried  $\text{LiCoO}_2$  sol in a dry nitrogen atmosphere (70 mg, 10 deg/min)

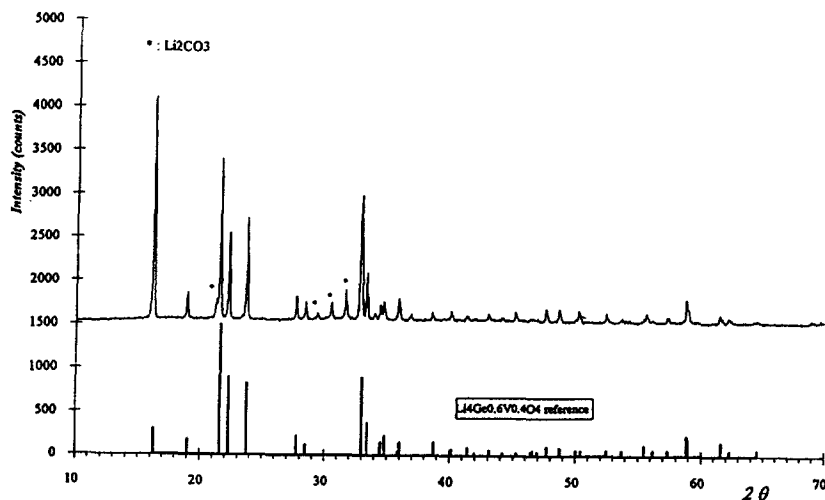


Fig. 7 X-ray powder diffraction pattern of  $.4\text{Li}_3\text{VO}_4/.6\text{Li}_4\text{GeO}_4$  powder prepared by removal of excess solvent at  $200^\circ$  and then firing at  $580^\circ\text{C}$  for 1 minute

$\text{LiCoO}_2$ . Similar results were obtained for the lithium manganese spinel samples. It is our hypothesis, based on the TGA and DSC measurements, that when sufficient sample is present, to compensate for heat losses, a spontaneous self sustained combustion synthesis takes place with the onset of the first exothermic decomposition at about  $200^\circ\text{C}$ . This combustion process does not require atmospheric oxygen to pyrolyze the organic species and therefore can be extremely efficient at eliminating carbon contamination.

**3.2 Electrolyte films.** We have recently studied the electrochemical properties of the ionic conducting elec-

trolyte  $4\text{Li}_3\text{VO}_4/.6\text{Li}_4\text{GeO}_4$  and determined that this system would be a very appropriate electrolyte in a high voltage system. [6] We decided that the simple spray pyrolysis technique developed for the cathode systems should be explored for the low temperature (i.e.,  $< 600^\circ\text{C}$ ) thin film synthesis of this material. One definite advantage of this electrolyte system is that small changes in stoichiometry have only minimal modifications on the conductivity and do not result in multiple phases. Initial experiments using sols prepared from lithium nitrate, germanium tetrachloride and vanadium tetrachloride in propylene glycol did not yield a single phase material even after annealing at  $800^\circ\text{C}$ . However, after eliminating all residual chloride with a silver nitrate titra-

tion the thermal decomposition of the sol with a composition of  $.4\text{Li}_3\text{VO}_4/.6\text{Li}_4\text{GeO}_4$  resulted in single phase material at temperatures as low as  $500^\circ\text{C}$ . In Figs. 7 and 8 are shown powder X-ray diffraction patterns of  $.4\text{Li}_3\text{VO}_4-.6\text{Li}_4\text{GeO}_4$  powder, and thin film sprayed onto an aluminum foil substrate. No annealing is required to obtain the desired phase; however, residual  $\text{Li}_2\text{CO}_3$  is usually obtained in the powder synthesis or if spraying is done onto a substrate at less than  $400^\circ\text{C}$ .

#### 4. Conclusions

We have demonstrated that it is possible to prepare thin film solid state battery components by a simple chemical process. In addition, since the desired phases are rapidly prepared at low temperatures the risk of interdiffusion between the desired phases is diminished. The solid state electrolyte  $.4\text{Li}_3\text{VO}_4-.6\text{Li}_4\text{GeO}_4$  has been prepared as a thin film onto a variety of substrates including  $\text{LiCoO}_2$  with no sign of substrate decomposition. In order to use this simple spray system to generate a working battery it is necessary to deposit an anode material that is also air stable and able to reversibly intercalate lithium at a low voltage relative to lithium metal. Our future research is aimed in this direction.

#### 5. Acknowledgements

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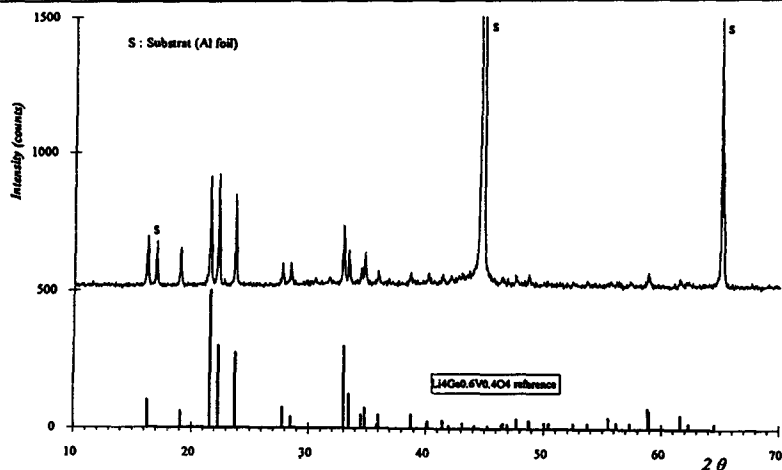


Fig. 8. X-ray powder diffraction pattern of thin film  $4\text{Li}_3\text{VO}_4/.6\text{Li}_4\text{GeO}_4$  deposited on an Al substrate (spray onto  $500^\circ\text{C}$  substrate)

## 6. References

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