Thin-film cathodes for secondary lithium batteries

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Abstract

We have prepared thin films of the active cathode materials $LiCoO_2$ and $LiMn_2O_4$ by chemical techniques. Low pressure chemical vapor deposition was successful at readily preparing $LiCoO_2$ at temperatures ranging from 450 to 650 °C; however, in order to prepare the spinel phase $LiMn_2O_4$ temperatures greater than 600 °C were required. The use of a spray pyrolysis technique was successful in preparing both $LiCoO_2$ and $LiMn_2O_4$ at substrates heated to temperatures as low as 400 °C. This temperature was probably not the actual synthesis temperature since thermal gravimetric experiments tend to indicate that our sol was capable of combustion synthesis.

Keywords: Secondary lithium batteries; Thin-film cathodes; Transition metal oxides

1. Introduction

The most recent candidates as cathodes for secondary lithium batteries are a family of lithiated transition metal oxides. These compounds all show high potentials versus a lithium anode (minimum of 3 V), are air stable in the fully lithiated state, and can show very good reversibility. The three compounds that are of most interest today are $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$. These compounds are well known in their normal high-temperature crystalline state and recently there have been reports of low-temperature phases showing modified structures and different electrochemical behaviors [1,2]. We have been interested in preparing thin films of the high-temperature electrochemically active compounds for a variety of battery applications.

Although in the literature there are various reports of physical vapor deposition techniques (laser ablation [2], ion beam evaporation [3] and reactive sputtering [4]), we felt there were particular advantages to using a chemical process to deposit thin films of these lithiated transition metal oxides. Specifically we felt that the chemical techniques would allow us to directly prepare the crystalline compound desired and allow us a wide control over the morphology of the material prepared. We have explored two entirely different chemical processes: chemical vapor deposition and polymeric decomposition (spray pyrolysis). Both of these techniques can readily prepare the desired high-temperature crystalline phases of $LiCoO_2$ and $LiMn_2O_4$ at temperatures as low as 450 °C.

2. Experimental

2.1. Chemical vapor deposition (CVD)

Films were prepared in a low pressure, horizontal hot wall reactor. The basic design is outlined schematically in Fig. 1. The precursors were heated with heavy insulated heating tape via variable transformers. The flow of argon and oxygen was controlled by standard mass-flow control meters (Brooks 5850 E). The pressure inside the reactor was monitored within the range 1–100 torr, with a capacitance manometer (Vacuum General CML-21), and controlled via a feedback loop (Vacuum General 80-6B) to a throttle valve system (Vacuum General MDV-015). The vacuum within the system was maintained by a mechanical pump (Alcatel 2008A). The temperature within the reaction zone was maintained by controlling (Parlow MIC 2000) a Kanthal wire wound furnace. The substrates used were aluminum foil, nickel-rich steel foil (alloy 214, Haynes Int.) and silica slides. The transition metal precursors (cobalt(III) acetylacetonate: $Co(CH_3COCHCOCH_3)_3$ (Strem Chemicals), and (methylcyclopentadienyl)manganese tricarbonyl (Strem Chemicals) are both air-stable compounds that were used as obtained. The organometallic lithium precursors (*sec*-butyllithium [11% in cyclohexane] and *tert*-butyllithium [22% in *n*-pentane]) were obtained from Johnson Matthey. The cyclohexane or pentane were distilled off, prior to use, at a secondary pumping station. The third lithium source was the lithium complex of 2,2,6,6-tetramethylheptane-3,5-dione (THD) ob-
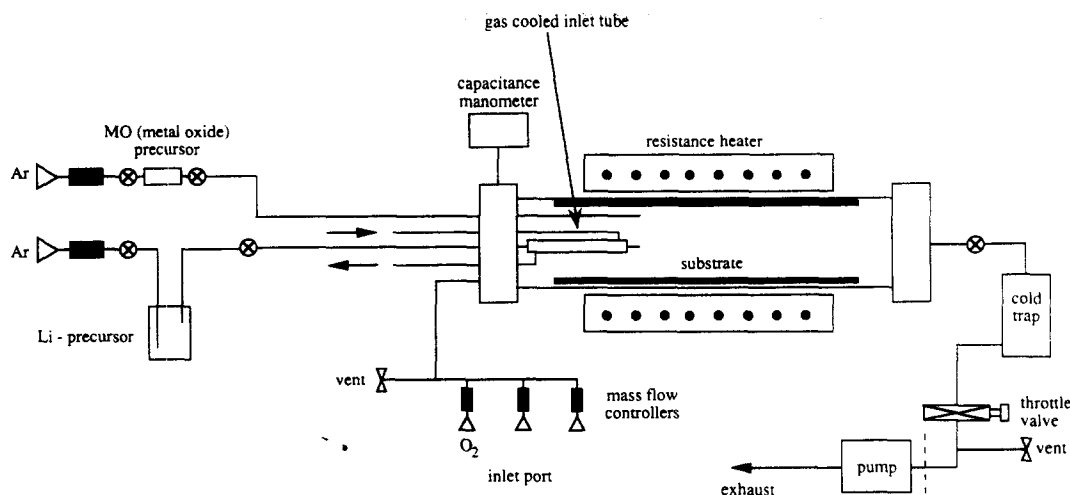
Fig. 1. Schematic diagram of low-pressure horizontal chemical vapor deposition system.

tained from Lancaster Synthesis. This complex was prepared by the dropwise addition of concentrated aqueous ammonia to a stirred ethanolic solution of LiCl and THD. The complex was removed by filtrating, rinsed and sublimed prior to use.

2.2. Spray pyrolysis

Sols of the desired lithiated metal oxide were prepared by reacting either cobalt(II) nitrate $(Co(NO_3)_2 \cdot 6H_2O)$ and lithium nitrate $LiNO_3$ or manganese(II) nitrate $(Mn(NO_3)_2 \cdot 6H_2O)$ and lithium nitrate with propylene or ethylene glycol (all compounds used as obtained from Aldrich Chemical Co.). The solutions (0.01–0.4 M) were heated under flowing nitrogen at temperatures ranging from 90 to 150 °C for 1 to 5 h. The sols were then kept at room temperature in closed vials until they were sprayed with an air-brush assembly (Olympus Medea) on to heated substrates. The temperature of the substrate surface was estimated with a chromel-alumel thermocouple. We verified the polycrystalline phases present by X-ray powder diffraction (XRD) (Philips XRD 3100) and determined the characteristics of the precursors by thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC) (Perkin-Elmer DSC-4), and Fourier-transform infrared spectroscopy (FT-IR) (Perkin-Elmer 16 PC FT-IR).

3. Results and discussion

3.1. Chemical vapor deposition

In order to determine the deposition parameters for chemical vapor deposition (CVD) we first prepared simple binary compounds. In the case of lithium deposition we rapidly abandoned the use of sec-butyllithium, since insufficient lithium was transported into

the reaction zone. It appears that for this compound sublimation is not an efficient process relative to decomposition and subsequent formation of lithium hydride. We were able to sublime tert-butyllithium and depending on the oxygen/tert-butyllithium ratio we could obtain either Li_2CO_3, Li_2O_2 or Li_2O at a substrate temperature of 475 °C. If we used an aluminum substrate at 550 °C we obtained AlLi. Regardless of the reaction conditions, Li–THD always reacted with oxygen to form Li_2CO_3.

The deposition of cobalt(III) acetylacetonate yields either Co_3O_4, CoO or Co depending on the substrate temperature and oxygen/cobalt ratio. In the case of (methylcyclopentadienyl) manganese tricarbonyl, depending on specific temperatures and oxygen/manganese ratios either MnO, Mn_3O_4 or Mn_2O_3 could be observed by XRD.

The crystalline ternary compound $LiCoO_2$ could be readily prepared at temperatures as low as 450 °C. In Table 1 are shown standard conditions for film growth. At 400 °C we always obtained material amorphous to XRD. Since we could easily obtain the desired material using the air-stable Li–THD complex, we abandoned detailed studies using tert-butyllithium and studied rate and morphology modifications using Li–THD. It is reasonable to say that although the morphology changed from dense optical type films at low growth rates (0.1–2 μm/h) to more porous films at high growth rates (2–10 μm/h) we always obtained $LiCoO_2$ as verified by XRD. This was not at all the case for the CVD of thin film $LiMn_2O_4$. In this case we usually obtained multiphase films containing Li_2MnO_3 and MnO as well as the desired $LiMn_2O_4$. We did obtain single-phase films of $LiMn_2O_4$; however, this was only when the substrate was at least 650 °C.

These preliminary studies indicated to us that thin films of $LiCoO_2$ and $LiMn_2O_4$ could be prepared by CVD; however, it is certain that films of $LiMn_2O_4$ are

Table 1
Reaction parameters for the preparation of $LiCoO_2$ thin films by chemical vapor deposition. T = substrate temperature, T_{Co} = temperature of cobalt reagent, F_{Co} = flow rate of cobalt-carrier gas (Ar), T_{Li} = temperature of lithium reagent, F_{Li} = flow rate of lithium-carrier gas (Ar), F_{O2} = flow rate of oxygen, and P = total reactor pressure in torr

Precursor	T (°C)	T_{CO} (°C)	F_{Co} (sccm)	T_{Li} (°C)	F_{Li} (sccm)	F_{O2} (sccm)	P (torr)	Phase
tert-Butyllithium	400	185	100	110	100	500	10	$LiCoO_2$ (amorphous)
Li–THD	500	180	50	280	100	500	50	$LiCoO_2$
Li–THD	450	175	50	280	100	500	50	$LiCoO_2$

not easy to prepare by CVD at low substrate temperature (i.e., less than 650 °C). The growth of thin-film polycrystalline $LiCoO_2$ is easy at any temperature greater than or equal to 450 °C. Modifications in growth conditions do not change the chemical composition but do effect the film morphology.

3.2. Spray pyrolysis

The sols of both $LiCoO_2$ and $LiMn_2O_4$ were sprayed directly on to heated substrates (aluminum foil, gold foil, Pyrex, and silica). The temperature of the heating plate was varied from 200 to 550 °C. At the lowest temperature the polymeric precursor is not entirely decomposed, whereas at the higher temperatures XRD indicates that the desired phase is prepared without additional annealing. Figs. 2 and 3 show the XRD spectra of $LiCoO_2$ and $LiMn_2O_4$ films respectively on aluminum foil substrates. These two films were sprayed on to substrates at ≈ 450 °C. The $LiCoO_2$ film was

subsequently annealed at 500 °C for 18 h to increase crystallite size and thus narrow the width of the diffraction peaks. In all cases, independent of the substrate temperature during the spraying operation, the desired high-temperature 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 only resulted in a larger grain size. The substrate temperature during spraying substantially modifies the morphology and adhesion of the films. As would be expected spraying at low temperatures results in highly porous films with poor mechanical strength. High temperature (i.e., > 400 °C) spraying results in dense, tough films with good adhesion to aluminum foil.

FT-IR spectra were performed on the sols after vacuum elimination at 80 °C of the excess propylene glycol serving as solvent. The resulting powders were mixed with KBr (1 wt.%) and pressed into standard 1 cm pellets. The spectrum of the $LiCoO_2$ precursor
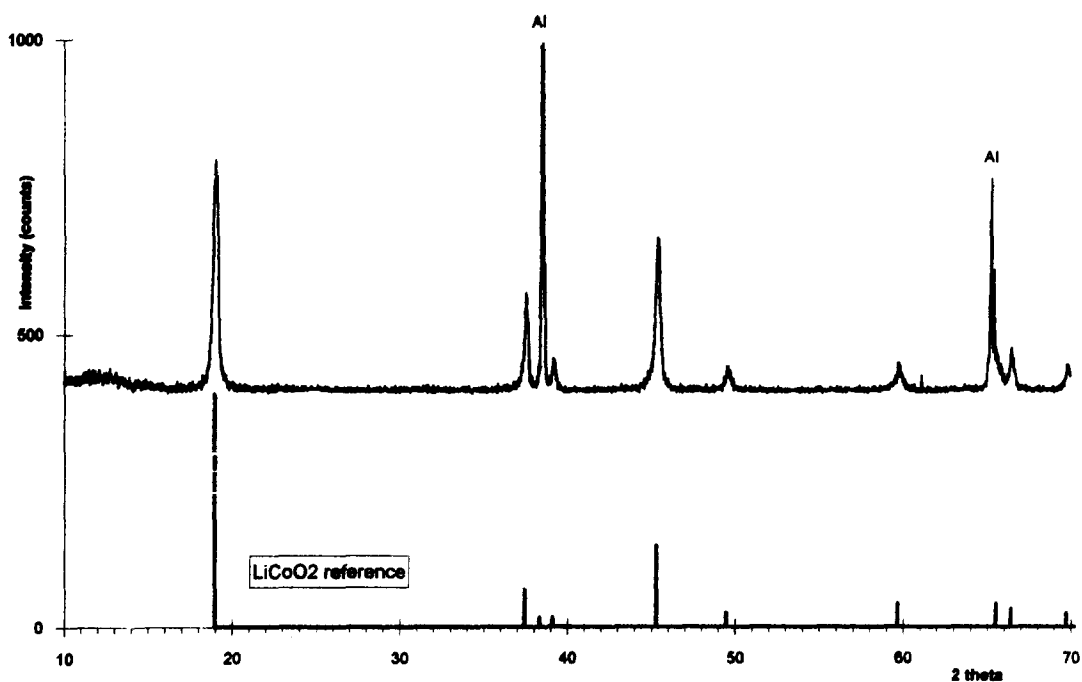

Fig. 2. X-ray powder diffraction spectrum of $LiCoO_2$ thin film on aluminum foil substrate; 500 °C anneal after spray on to 450 °C substrate.
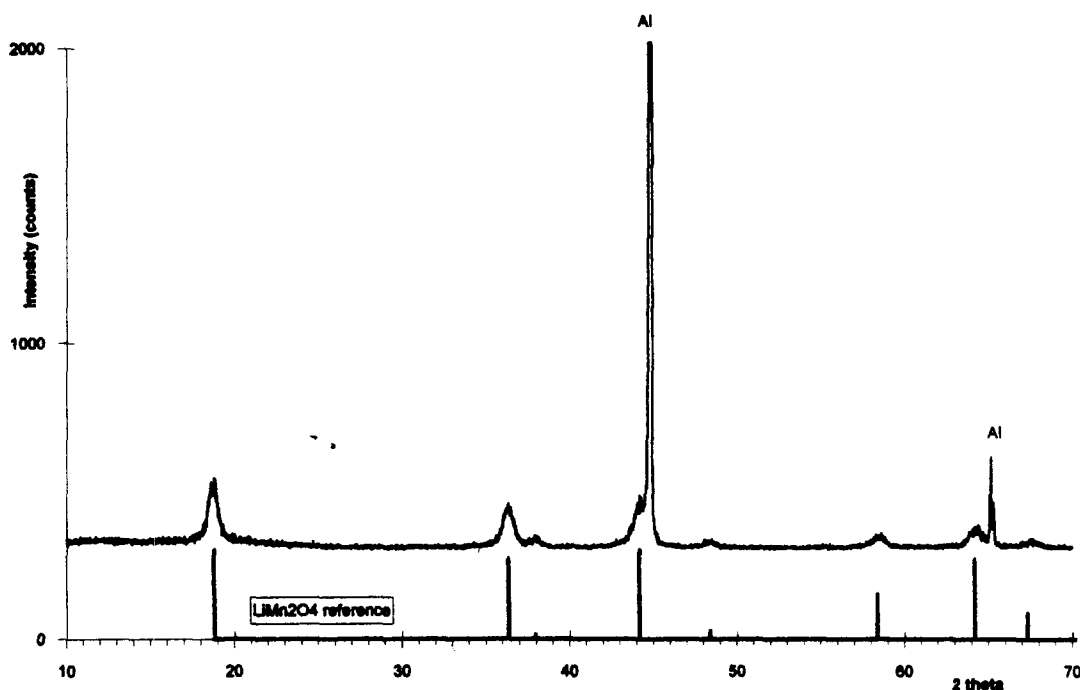
Fig. 3. X-ray powder diffraction spectrum of LiMn₂O₄ thin film on aluminum foil substrate; spray on to 450 °C substrate, no anneal.
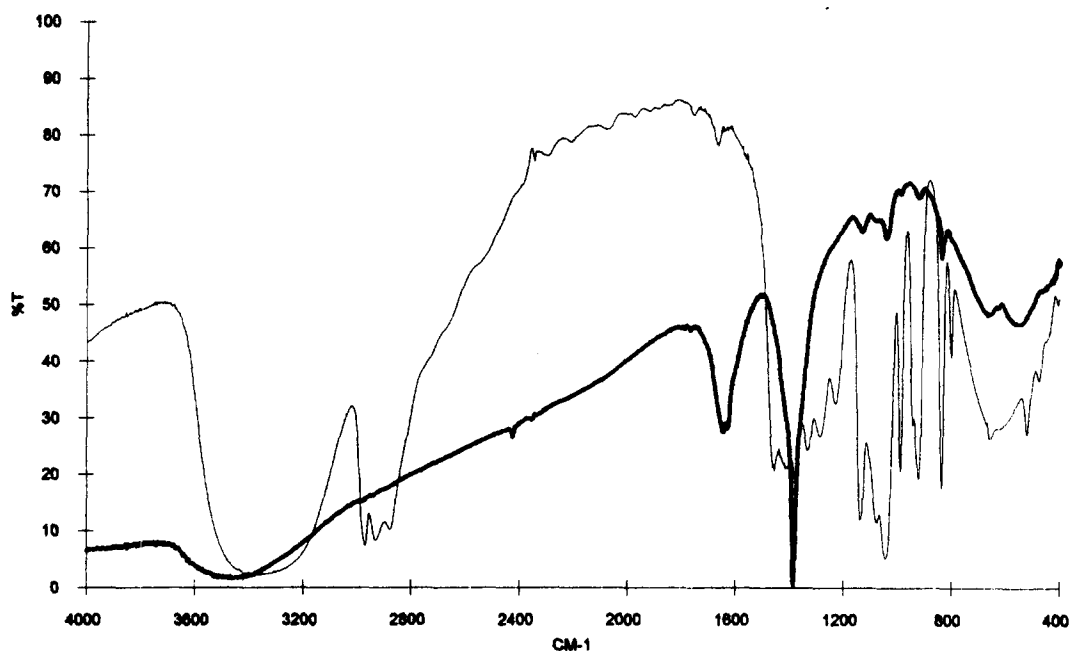

Fig. 4. FT-IR spectra of vacuum-dried LiCoO₂ precursor (———) and propylene glycol reagent (———).

is shown in Fig. 4. The most striking features are the strong carbonyl peak at 1640 cm⁻¹, and the loss in the CH peak present in the original glycol at 2860–2990 cm⁻¹. It is certain that the metal nitrates result in diol oxidation; however, the exact chemical nature of the remaining polymer-oligomer is not known at this time.

DSC and TGA were performed in an air atmosphere and the results are shown in Figs. 5 and 6, respectively. 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 (344 and 319 cal/gram). To better understand the decomposition reaction occurring in the synthesis process we also performed a TGA under nitrogen with a larger sample size (70 mg rather than the previous sample size of 13 mg). In this measurement an extremely rapid one-step decomposition occurs (see Fig. 7). XRD of the sample used in this experiment showed the
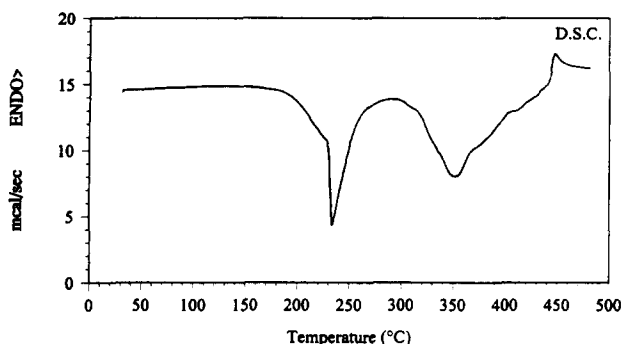
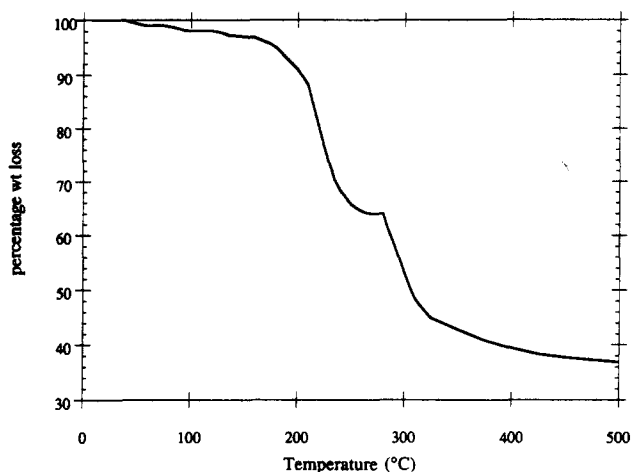Fig. 5. Differential scanning calorimetry data of vacuum-dried LiCoO₂ sol heated under an air atmosphere, 5.9 mg, 10 °C/min.

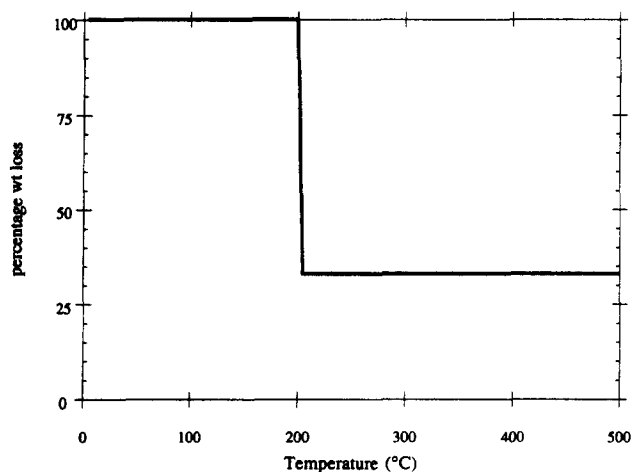Fig. 6. Thermal gravimetric analysis data of vacuum-dried LiCoO₂ sol heated under an air atmosphere, 13 mg, 10 °C/min.

Fig. 7. Thermal gravimetric analysis data of vacuum-dried LiCoO₂ sol heated under a dry nitrogen atmosphere, 70 mg, 10 °C/min.

material to be single-phase $LiCoO_2$. 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 °C. This combustion process does not require atmospheric oxygen to pyrolyze the organic species and, therefore, can be extremely efficient at eliminating carbon contamination.

4. Conclusions

Chemical techniques can be successfully used to prepare thin films of the active cathode materials $LiCoO_2$ and $LiMn_2O_4$. CVD can prepare thin polycrystalline $LiCoO_2$ over a wide temperature range (450–650 °C) with morphology dependent on specific reaction conditions. We had substantial difficulty preparing thin-film $LiMn_2O_4$ by CVD until higher substrate temperatures were used (at least 650 °C).

By using a spray pyrolysis technique, thin polycrystalline films of both $LiCoO_2$ and $LiMn_2O_4$ could be readily prepared with substrate temperatures less than 450 °C. Since a spontaneous combustion synthesis is probably occurring it is possible that higher temperatures are occurring on a microscale; however, this does not limit substrate use (excellent films thicker than 5 μm can be prepared on aluminum foil). Since the spray pyrolysis technique requires less hardware and simple inexpensive reagents, we feel it has several advantages over CVD. In addition, it gave us superior results for the preparation of thin film $LiMn_2O_4$.

Acknowledgements

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