



## Synthesis of Nanoscale Lithium-Ion Battery Cathode Materials Using a Porous Polymer Precursor Method

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Fine particles of metal oxides with carefully controlled compositions can be easily prepared by the thermal decomposition of porous polymers, such as cellulose, into which solutions containing salts of the desired cations have been dissolved. This is a simple and versatile method that can be used to produce a wide variety of materials with a range of particle sizes and carefully controlled chemical compositions. Examples of the use of this method to produce fine particles of  $\text{LiCoO}_2$  and  $\text{Li}(\text{NiMnCo})_{1/3}\text{O}_2$ , which are used in the positive electrodes of lithium-ion batteries, are shown. Experiments have demonstrated that materials made using this method can have electrochemical properties comparable to those typically produced by more elaborate procedures.

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This is a busy time in a number of areas within the materials research community. One of these involves the exploration of new materials for use in advanced lithium batteries. The search for new reactants to be used in their positive electrodes is especially active. Candidates are typically oxides containing one or more transition metal ions.

The evaluation of potentially interesting materials requires their synthesis, and a number of different methods are currently being used for that purpose. These range from the traditional ceramic preparation methods in which several oxides, sometimes also including oxyfluorides, that, together, include the ions that are desired in the final product, are mixed together, pressed, sintered, and annealed in order to allow interdiffusion to produce products with the desired uniform compositions and crystal structures. This is generally followed by the use of mechanical methods to produce the required particle size.

Recently, a variety of “wet chemistry” and hydrothermal methods have also been developed and used for this purpose in a number of laboratories. Each of these has its advantages and limitations. Some are relatively simple, whereas others are quite elaborate, involving careful control and multiple critical steps. A number of these methods also require subsequent processing to produce the desired particle sizes, shapes, and crystallographic defect concentrations.

The general goal is the same, to produce a product of a specific phase that has the desired particle sizes and shapes without local compositional and/or crystallographic inhomogeneities. Fine particle sizes and carefully controlled compositions are generally desired in order to obtain good kinetics and capacities in electrochemical applications.

The purpose of this paper is to describe a relatively simple, inexpensive and versatile method that can also be used for this purpose. It will be seen that it can produce a wide variety of compositions with controlled particle sizes, and with relatively fine control over their chemical constitution.

This method, which we describe as a “porous polymer precursor” procedure, involves the incorporation of a solution containing the ions desired in the final product into the structure of a simple polymer, and then decomposition of the polymer at modest elevated temperatures in an oxidizing environment to form the desired oxide product.

### Prior use of the polymer precursor method to produce ceramics

It was shown by Bernard Hamling, starting in the 1960's, that it is possible to produce metal oxide fibers, textiles and shapes by immersing a polymer that can absorb water, such as cellulose, in an aqueous solution containing metal salts, and then decomposing it by heating in air to form a solid containing the corresponding metal oxides.<sup>1,2</sup> The primary examples involved imbibing aqueous solu-

tions of  $\text{AlCl}_3$  or  $\text{ZrOCl}_2$  into cellulose fibers, followed by heating them in air to produce fibers and shapes of  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ .

This work was done at the United Carbide Corporation research laboratory, but Union Carbide was not interested in pursuing this method for the production of oxides. Hamling acquired the rights to these patents, and established Zircar Products, Inc. to pursue their commercialization. In 2000 this company was divided into three successor companies to specialize in different product lines, including zirconium and aluminum oxide fibers and ceramic shapes for a number of applications. By careful control of the processing conditions and the polymer precursor, they are able to produce materials with remarkably good mechanical properties.

This method was subsequently used to produce powders of materials in the sodium – aluminum – oxygen system related to sodium beta alumina, as well as a potassium analog for study as possible solid electrolytes.<sup>3</sup> In that case the polymer was cellulosic filter paper, and the products were powders. There have subsequently been several reports of the use of other polymer pyrolysis methods (Refs. 4–6).

### The production of well-defined materials of potential use as battery electrode reactants

By control of relevant parameters, this method can be used to produce a wide variety of materials of potential interest as battery reactants by soaking readily available inexpensive cosmetic cotton swabs, which are high purity cellulose, in solutions of nitrate salts. Species from the aqueous salt solutions enter microcrystalline domains of the D-glucose polymer chains in the cellulose, causing the polymer to swell.<sup>7</sup>

Upon heating in air, a series of processes take place. Water is first given off, followed by light fragments from the polymer structure. This is followed by the oxidation of the carbon content to form species that also go into the gaseous environment. The residual cations present react with the air in the environment to form fine solid oxide particles, which nucleate and grow upon the structure of the former cotton fibrils.

The oxide particles are initially very small, and essentially replicate the microstructure of the polymer. At higher temperatures they gradually become larger and begin to sinter together.

Typical features of this process are illustrated in Figs. 1a–1d.

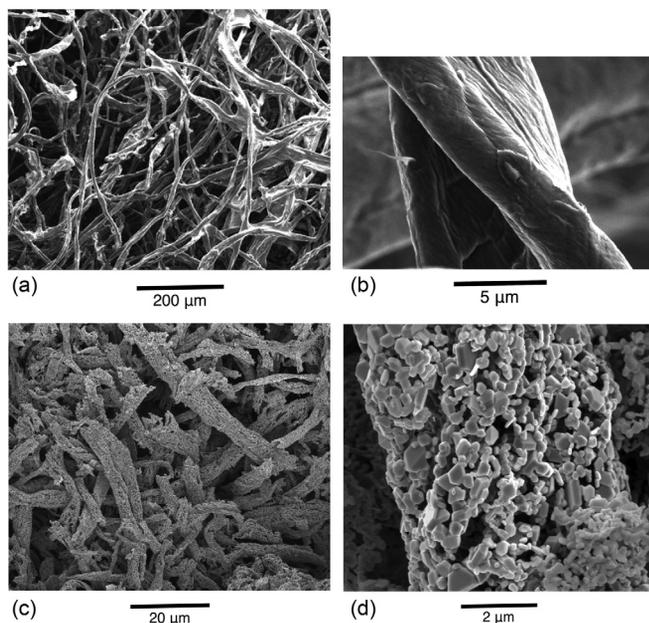
### Advantages and controllable parameters

There are a number of distinct advantages of this inherently simple and inexpensive materials preparation method. The chemical composition of the final oxide product is very uniform, and is determined by the composition of the aqueous solution that is dissolved by the polymer. There are essentially no contaminants introduced by the high purity cellulose, and the cationic species from the salt are thoroughly mixed at the atomic level. It is possible to determine the cation content in the oxide product with considerable precision by control of the chemical composition of the aqueous solution.

A wide range of oxide compositions can be produced, limited only by the availability of appropriate water-soluble salts. By

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**Figure 1.** (a) The microstructure of dry cotton, as seen in a scanning electron microscope at a relatively low magnification. (b) The microstructure of cotton at a higher magnification. (c) SEM picture of the microstructure after salt absorbed into the cotton structure is converted into oxide particles. (d) Higher magnification SEM picture showing individual  $\text{LiCoO}_2$  particles formed on a single polymer fiber.

control of the thermal cycle it is possible to influence the size and uniformity of the oxide particles that are formed. Although they are originally formed in a structure related to the microstructure of the cotton polymer, relatively light mechanical grinding will cause them to separate from each other.

The concentrations of the salts in the solution influence the amount of oxide formed, and the size of the resulting particles. As mentioned above, the commercial production of solid materials using this process that have good mechanical properties requires the use of concentrated salt solutions. The use of dilute solutions, on the other hand, results in a rather porous product with very fine particles that are relatively widely spaced from each other. The thermal treatment also has an important influence upon the characteristic of the products that are formed.

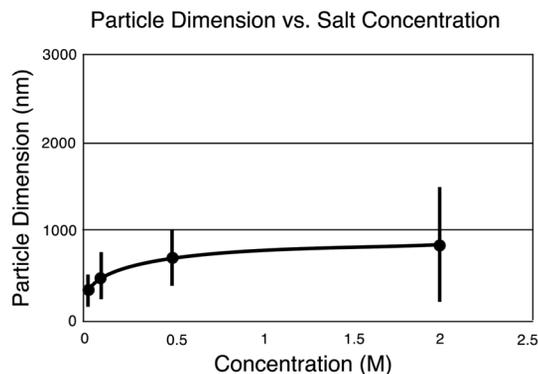
### Other variants

In addition to the use of aqueous solutions and cellulose, other variants are also possible. The important issues are simple. Salts containing the ions desired in the final product must be soluble in a liquid solvent that will be imbibed by a polymeric material that will decompose upon heating. As an example, phosphoric acid solutions could be used in order to produce solid phosphates. Organic solvents, such as ethanol and methanol, can also be used to dissolve materials containing the cations that are desired in the final product if there are no appropriate salts that are readily soluble in water.

As a further variation, the gaseous environment can be modified, with implications upon the rates at which the particles form, as well as their composition. In the examples described here, the precursor materials were heated in air, but other atmospheres can also be used to control the oxygen stoichiometry, or if non-oxide products are desired.

### Examples

*Investigation of process variables to produce fine particles of  $\text{LiCoO}_2$ .*—This method was used to produce particles of  $\text{LiCoO}_2$ , a common lithium cell positive electrode reactant. A group of experiments were performed in order to explore the influence of several



**Figure 2.** Influence of the salt concentration upon the final particle size.

variables in the process. In all cases, cosmetic cotton swabs obtained from a local drug store were soaked in solutions of  $\text{LiNO}_3$  and  $\text{Co}(\text{NO}_3)_2$ , purchased from Sigma-Aldrich, in de-ionized water in a 1:1 molar ratio.

The resulting materials were ground in a simple mortar and pestle, and the particle morphologies and sizes were determined from images obtained by the use of a scanning electron microscope. Between 80 and 150 particles were manually counted and measured in each case. X-ray diffraction experiments resulted in sharp lines at positions that confirmed the formation of the  $\text{LiCoO}_2$  phase in all cases.

*Influence of the salt concentration.*—In order to investigate the influence of the salt concentration, solutions with total salt concentrations of 0.025, 0.1, 0.5 and 2 M were employed.

In each case, 15 g of cotton swabs were soaked in these solutions for 3 h. They were then squeezed to remove excess liquid. The damp cotton was placed in a box furnace and heated in air at a rate of  $100^\circ\text{C}$  per hour to a temperature of  $400^\circ\text{C}$ . This rate was chosen in order to ensure controlled evaporation of the incorporated water and controlled oxidation of the cellulose, instead of combustion.

After cooling, the resulting material was gently hand ground and returned to the furnace. It was then heated at the same rate to a final temperature of  $900^\circ\text{C}$ , which was maintained for 4 h. Subsequently, the product was taken from the furnace and allowed to cool in air to room temperature.

This two-step heating procedure was used, rather than continuous heating, to ensure homogeneity of the resulting material. Fine particles of relatively uniform size and shape were produced in all cases, but their size depended upon the salt concentration in the soaking solution. This is illustrated in Fig. 2. In this figure, as well as in those to follow, the error bars indicate one standard deviation above and below the mean values.

*Influence of the maximum temperature.*—Similar experiments were undertaken in which the maximum temperature was varied, to 850, 900, 950 and  $1000^\circ\text{C}$ . In each case, the maximum temperature was maintained for 4 h. This parameter had a relatively large effect upon the particle size, as can be seen in Fig. 3.

*Influence of the duration of the holding time at the maximum temperature.*—Another parameter that was investigated was the influence of the holding time at a single maximum temperature. Samples were held at  $900^\circ\text{C}$  for 2, 4, 8 and 12 h. The influence of this factor upon the final particle size is shown in Fig. 4.

*Influence of soaking time in the salt solution.*—A group of experiments were performed in which a solution of 0.5 M concentration was used, and the cotton soaking time was varied from 1 min to 24 h. These samples were subjected to the standard two-step heating cycle to a maximum temperature of  $900^\circ\text{C}$ , which was maintained for 4 h. There was essentially no influence of the soaking time

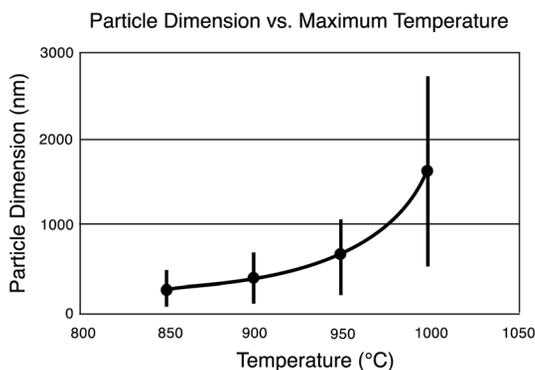


Figure 3. Influence of the maximum temperature upon the particle size.

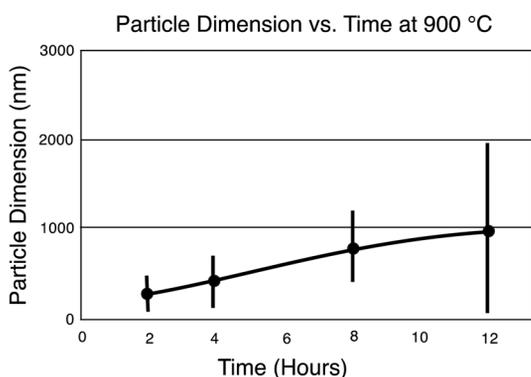


Figure 4. Influence of the holding time at maximum temperature upon the final particle size.

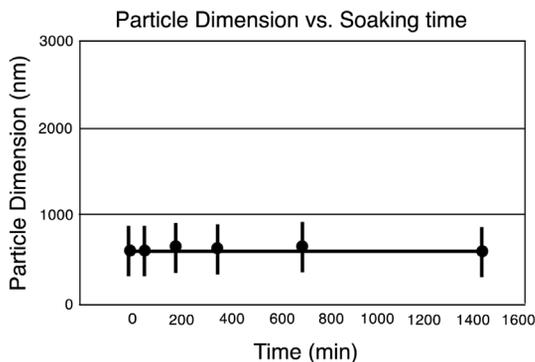


Figure 5. Influence of the soaking time upon the particle size.

within this range, as shown in Fig. 5. This means that the salt solution penetrates into the polymer structure of the cellulose very fast.

*Influence of the addition of glucose to the salt solution.*—The possibility that the presence of 1 M D-glucose in a 0.5 M salt solution might have a significant influence on either the particle size or the size distribution was explored. No significant influence was observed in this experiment.

*Fine particles of  $\text{Li}(\text{NiMnCo})_{1/3}\text{O}_2$ , (NMC).*—Another positive electrode reactant that has also been widely investigated in recent years for use in lithium-ion batteries is  $\text{Li}(\text{NiMnCo})_{1/3}\text{O}_2$ . This is sometimes simply called (NMC). Nitrate salts, purchased from Sigma-Aldrich, were also used in this case, as were common cosmetic cotton swabs obtained from a local drug store.

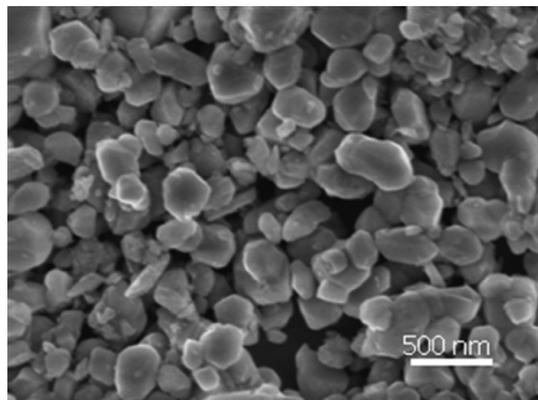


Figure 6. NMC particles resulting from the use of the porous polymer precursor process.

In this case, as solution containing 0.5 M  $\text{LiNO}_3$ , and 0.167 M each of  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Mn}(\text{NO}_3)_2$  and  $\text{Co}(\text{NO}_3)_2$  was used. The thermal treatment was essentially the same as that used for the formation of  $\text{LiCoO}_2$ , with a maximum temperature of 900°C for 6 h. X-ray diffraction experiments also gave sharp lines in this case at positions that confirmed the presence of the desired phase. The general size and shape of the particles resulting from this treatment are illustrated in Fig. 6.

### Electrochemical experiments

Electrochemical experiments were performed to demonstrate the electrochemical performance of the materials made by the use of this process.

In both cases, electrodes were prepared by making slurries of 76% active material, 14% conducting carbon black, and 10% PVDF binder in an NMP solvent. Slurries were doctor-bladed onto aluminum foil, dried at 110°C for 1 h, and then pressed to form even layers. Electrodes were cut out and put into coin cells, which were assembled within an argon-filled glove box with low oxygen and water contents.

Lithium metal foil was used as the negative electrode, and a 1 M solution of  $\text{LiPF}_6$  in EC/DEC, 1:1, from Ferro Corporation was used as the electrolyte. The separator was polypropylene-based Celgard 2321. Experiments were made by use of a BioLogic VMP3 multi-channel potentiostat-galvanostat.

*Capacity of  $\text{LiCoO}_2$  material as a function of discharge rate.*—Brief experiments were performed to investigate the discharge capacity of the  $\text{LiCoO}_2$  material synthesized as described above at a series of different rates, limiting the compositional change to 0.5 Li per formula unit. The results, measured on samples with a particle size of about 500 nm are shown in Fig. 7.

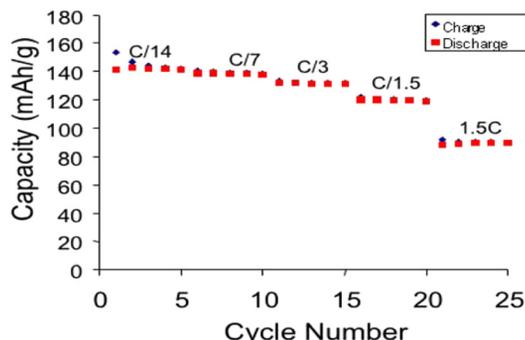
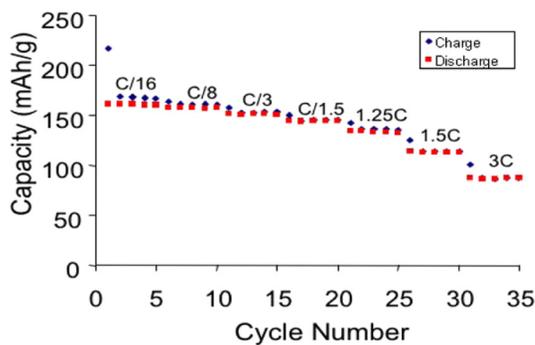


Figure 7. (Color online) Capacity of  $\text{LiCoO}_2$  electrodes as a function of the charge and discharge rate.



**Figure 8.** (Color online) Capacity of  $\text{Li}(\text{NMC})_{1/3}\text{O}_2$  as a Function of Charge and Discharge Rate.

It is seen that the capacity, measured over a voltage range from 3 to 4.3 V, at a low rate, 20 mA/g, is over 140 mAh/g, which is comparable to the theoretical limit. It decreases with increasing discharge rate, as expected, with values that are comparable to those in other studies that have shown the superior performance of sub-micron particles.<sup>6</sup>

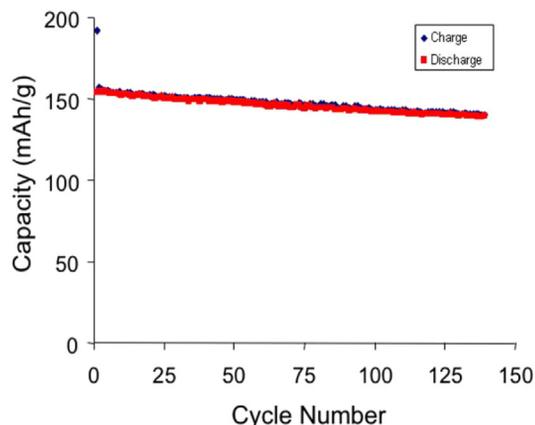
Although these experiments indicate no apparent decline in capacity with the number of cycles at the several rates, they were performed over only a small number of cycles in each case. Reliable information about the capacity as a function of the number of cycles would require more extensive testing at each individual rate.

*Electrochemical performance of NMC material.*—Limited experiments were also performed to evaluate the discharge capacity of the NMC material heated to 900°C for 6 h as a function of rate. In this case the average particle size was smaller, about 200 nm. The results are shown in Fig. 8. The initial discharge capacity, measured at a voltage range from 3.3 to 4.3 V, was over 160 mAh/g at a current of 20 mA/g. This is comparable to, or higher, than values found in the literature for materials prepared by other methods.<sup>7–15</sup>

As mentioned above, reliable information about the capacity as a function of the number of cycles requires more extensive testing at each individual rate. One example of the variation of the capacity during extended cycling is shown in Fig. 9. It can be seen that this material exhibited excellent cycle life, retaining more than 90% of its original capacity after 150 cycles at a C/3 rate. This is comparable to, or better than, the best values in the literature.<sup>16</sup>

### Summary and Discussion

This paper describes a very simple, versatile, and relatively low cost method for the preparation of a wide variety of materials in fine particle form that is also readily scalable. The experimental parameters can be readily manipulated to provide desired compositions and particle sizes.



**Figure 9.** (Color online) Variation of the Capacity of  $\text{Li}(\text{NMC})_{1/3}\text{O}_2$  Electrodes as a Function of Cycle Number at a C/3 Rate.

Experiments have demonstrated that submicron-size particles of two well-known lithium battery positive electrode reactant materials can be easily produced in this manner. Electrochemical measurements have shown that their properties are comparable to, or even better, than those that can be achieved by the use of other methods.

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