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One step synthesis of lamellar *R-3m* $LiCoO_2$ thin films by an electrochemical–hydrothermal method

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ABSTRACT

In this study, we report the synthesis of lamellar *R-3m* $LiCoO_2$ thin films electrodes for lithium rechargeable batteries by a single step method based on an electrochemical–hydrothermal synthesis in a concentrated LiOH solution with a cobalt salt. This process combines the effect of temperature (between 150 °C and 200 °C), pressure and galvanostatic current. The obtained films were not annealed after the electrochemical–hydrothermal synthesis.

For the first time, the theoretical study of the potential–pH diagram of cobalt was carried out at high temperature and high concentration. These calculations show that a pH value higher than 12 is necessary to avoid the direct precipitation of cobalt hydroxide $Co(OH)_2$ inside the solution. An improvement of the soluble species stability with an increase of the temperature and a decrease of the cobalt concentration is predicted. The influence of the deposition conditions (temperature and concentration) at a constant current density was experimentally studied. X-ray diffraction (XRD) shows the formation of well-crystallized $LiCoO_2$ thin films. Raman spectroscopy confirmed the achievement of the electrochemically active *R-3m* $LiCoO_2$ phase without any trace of the *Fd3m* phase at temperatures as low as 150 °C. Electrochemical measurements demonstrate good performances of the material synthesized between 150 °C and 200 °C with better capacity retention at higher temperature.

1. Introduction

The considerable development of microelectronics and the miniaturization effort for the past two decades led to the development of microscale lithium-ion batteries (so-called microbatteries) which are realized by the successive deposition of thin layers of active materials and solid electrolyte mainly by PVD processes (Physical Vapour Deposition) [1,2]. $LiCoO_2$ is a main material as positive electrode for these batteries. Indeed, $LiCoO_2$ intensively studied since 1980 [3] exhibits a high specific energy (137 mAh/g between 3 and 4.2 V versus Li^+/Li), an excellent cycle life [4–6] and a high electronic conductivity. Thin films of $LiCoO_2$ are currently mainly realized by sputtering [7,8] but because of its low rate of deposition (10 nm/mn) and its limiting conditions of use (high vacuum, high tension, etc.) this technique remains expensive. Moreover, a thermal post-treatment (>500 °C) is always necessary to obtain the electrochemically active phase of $LiCoO_2$ (lamellar *R-3m*) which limits the choice of substrates to thermally resistant materials. New deposition methods, more particularly wet chemistry methods like sol/gel [9–11] or hydrothermal synthesis [12–15], are studied to overcome these drawbacks. However, the sol/gel route also requires a post annealing treatment at relatively high temperature (~600 °C) [16]. Moreover, the decomposition of organic compounds makes dense films difficult to obtain.

Hydrothermal process seems to be a convenient synthesis method to deposit $LiCoO_2$ thin films at moderate temperature [12–15]. In the reported studies, the electrolyte solution used for the deposition is very alkaline – LiOH between 1 mol l^{-1} and 6 mol l^{-1} – and a cobalt metallic substrate is often used as a source of cobalt ions The deposition time remains very long, commonly 20 h. The use of H_2O_2 as an oxidant is reported to increase the oxidation rate of cobalt [17] and only few studies report the use of a current density (few mA cm^{-2}) to oxidize cobalt ions [18–21]. The latter technique allowed the direct deposition of well crystallized *R-3m* $LiCoO_2$ on metallic substrate (Pt, Co, etc.). Watanabe et al. [18] conducted experiments in a flow cell requiring a constant provision of fresh electrolyte but other studies were done in closed cell [21]. Only few studies exhibit electrochemical results [19,21] showing a severe capacity fade during cycling [19].

In this study, thin films of $LiCoO_2$ are synthesized via the electrochemical–hydrothermal route in a closed stainless steel autoclave without any electrolyte circulation and very short depo-

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sition time. The cobalt ion source is a cobalt salt dissolved in a LiOH alkaline solution which allows the $LiCoO_2$ deposition on various substrates (titanium foil, protected silicon wafer, etc.).

In a first step, a theoretical study of the potential–pH diagram of cobalt species in the range 150–200 °C has been undertaken to determine the evolution of the predominance domains of the various cobalt species as a function of both temperature and concentration.

Structure and electrochemical properties of the obtained thin films have been investigated.

2. Experimental

$LiCoO_2$ thin films were synthesized by an electrochemical–hydrothermal process on a titanium foil substrate (25 mm × 25 mm, Goodfellow, ≥99.6%) or a protected wafer substrate ($Si/SiO_x/Ti/Pt$). The back of the silicon wafer is protected by an epoxy polymer thin film which is chemically and thermally resistant. The precursor bath was composed of a cobalt salt ($Co(NO_3)_2{\cdot}6H_2O$, ACS Reagent ≥98%) dissolved in a concentrated solution of lithium hydroxide ($LiOH{\cdot}H_2O$, ACS Reagent ≥98%) in deionised and deoxygenated water. The synthesis was conducted in a 1L stainless steel autoclave with a polyfluoroethylene (PTFE) vessel adapted to the pressure. The whole was thermo-regulated by a Parr reactor controller 4848 (Fig. 1) and the temperature was varied between 150 °C and 200 °C. The substrate was placed vertically at 12 mm of the platinum counter electrode. The electrolysis conditions at constant current density (1 mA cm^{-2}) were monitored by a Voltalab PST050 galvanostat/potentiostat (Radiometer Analytical). The resulting thin films were rinsed three times in distilled water to eliminate the residual precursor solution and then dried in air. No post-synthesis heat treatment was applied.

The crystal structure of $LiCoO_2$ thin films was investigated with a Brüker D8000 diffractometer using Cu Kα radiation. The formation of the *R-3m* $LiCoO_2$ phase was confirmed by Raman spectra measured with a LaBRAM HR 800 (Jobin-Yvon-Horiba) Raman micro-spectrometer including Edge filters and equipped for signal detection with a back illuminated charge coupled device detector (Spex CCD) cooled by Peltier effect to 200 K. A He:Ne laser (632.8 nm) was used as the excitation source. Morphology and surface aspects were observed with Scanning Electron Microscope (SEM) Hitachi 4000/4100. The thickness of the deposit was determined by SEM images.

Galvanostatic cycling and linear sweep voltammetry experiments were carried out on these electrodes in 2032 coin cells at 20 °C. Lithium foil (Chemetall, battery grade) was used as negative electrode. The electrolyte was a 1:1:3 mixture by volume of ethylene carbonate (EC), propylene carbonate (PC) and dimethyl carbonate (DMC) containing 1 mol l^{-1} of $LiPF_6$. Then the positive electrode consisted of the thin film of $LiCoO_2$ obtained by electrochemical–hydrothermal synthesis. Coin cells were assembled in an argon-filled glovebox. Cyclic voltammograms were carried out at 5 μV s^{-1} between 3 and 4.2 V (versus Li^+/Li), galvanostatic cycling was done at a C/5 rate between 3 and 4.2 V.

3. Results and discussion

3.1. Theoretical study of the potential–pH diagram of cobalt

The thermodynamic constants and the predominant species in drastic environment (high alkalinity, high temperature, etc.) are subject to controversy. For simplicity, we choose to consider common species and the assumptions adopted by Pourbaix in 1963 [22] which is the reference in potential–pH diagrams calculation.

The equilibrium equations of chemical species in the $Co–H_2O$ system were calculated from the Nernst Equation (2) where E is the potential (V), E^0 the standard potential of the redox couple (V), R the gas constant (8.3146 J mol^{-1} K^{-1}), T the temperature (K), n the number of electrons involved in the redox reactions, F the Faraday constant (96485 C), a the activity of the considered species and γ_i the activity coefficient and $[i]$ the concentration.

$$xOx + ne^- \leftrightarrow yRed \tag{1}$$

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{ox}^x}{a_{red}^y} \tag{2}$$

$$a_i = \gamma_i \times [i] \tag{3}$$

Considering the high alkalinity of the solution, activity of protons H_3O^+ was considered to be equal to their molar concentration and the pH was calculated from the H_3O^+ concentrations values. Moreover, the activity of solid species was considered to be equal to 1. Considering the high concentration of cobalt species in solution (above 1 mol l^{-1}), the activity should be calculated with equation (3). The calculation of the activity coefficient γ_i is very complex in such solution. Therefore, despite the high cobalt species concentration, we consider that the activity of cobalt species is equal to their molar concentration. These rough estimates allow a simpler calculation of the potential–pH diagram. Thereof, considering these approximations, the potential–pH diagram is used to predict the evolution of the stability domains of the various cobalt species as a function of pH and temperature but, not to determine quantitatively their exact limits.

Based on these formulas, the relationship between the potential and the pH (related to the LiOH concentration in these experiments) was calculated as a function of two parameters: the temperature and the cobalt concentration. The results are summarized in Table 1.

The potential–pH diagram of a solution at 1 mol l^{-1} of cobalt species, at 150 °C and 200 °C are reported respectively in Fig. 2a and b. These diagrams show that the pH value has to be high (higher than 12) to avoid the precipitation of $Co(OH)_2$ which is insoluble in the solution. An increase of the temperature tends to improve the stability of the aqueous species $HCoO_2^-$ and to decrease the pH of the predominance limit of the cobalt hydroxide. The evolution of the potential–pH diagram with the cobalt concentration is reported in Fig. 3. The decrease of the cobalt concentration shifts the predominance limit of $Co(OH)_2$ and $HCoO_2^-$ to lower pH values. These calculations then show a tendency to decrease the limit pH value of the predominance domain of $Co(OH)_2$ and $HCoO_2^-$ with an increase of the temperature and a decrease of the cobalt concentration.

Chivot et al. [23] adopted different assumptions and published revised Pourbaix diagrams between 25 °C and 150 °C at concentrations from 10^{-6} to 10^{-2} mol kg^{-1}. This work is based on revised thermodynamic data and a correlation between the chemical properties at 25 °C and those observed at higher temperatures established by Criss et al. in 1964 [24,25]. This calculation method is obviously more precise than ours but leads to the same variation of the predominance domains of cobalt species with both the concentration and the temperature. Chivot does not take into account the same species as Pourbaix but founds that the soluble species present at high pH values are $Co(OH)_3^-$ and $Co(OH)_4^{2-}$ which are similarly to $HCoO_2^-$ containing Co(II) ions. It is important to notice an increase of the stability domain of Co_3O_4 found by Chivot which seems to be more in accordance with the formation of Co_3O_4 impurities during our own experiments in comparison with the very narrow stability domain found in our calculations. Moreover, pressure is never taken into account in both calculation methods which increases the approximation of the potential–pH diagrams obtained.