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Synthesis of [Co/LiF/C] nanocomposite and its application as cathode in lithium-ion batteries

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ABSTRACT

[Co/LiF/C] nanocomposite has been synthesized by pyrolysis of a cobaltocene/LiF mixture at 700 °C in a closed reaction vessel under argon atmosphere. The morphology, structure and composition of the material was characterized by Raman spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen physisorption measurement (BET) and elemental analysis. The composite is comprised of hexagonally closed packed (*hcp*) and face centred cubic (*fcc*) cobalt nanoparticles and LiF, which are embedded in a matrix of graphitic nanostructures. The composite has both micro- ($0.05\,cm^3\,g^{-1}$) and mesopores ($0.1\,cm^3\,g^{-1}$), and exhibits a BET surface area of $177\,m^2\,g^{-1}$. Electrochemical characterizations were performed versus lithium to determine the capacity, cyclic stability and to investigate the reaction mechanism. At a given current density of $27.8\,mA\,g^{-1}$ the composite electrode exhibits an initial specific discharge capacity of $152\,mAh\,g^{-1}$ (based on cobalt and fluorine content) which stabilizes at about $170\,mAh\,g^{-1}$ over 70 cycles.

1. Introduction

In state of the art lithium-ion batteries, lithium ions are stored in the electrode materials by intercalation processes. Although this mechanism allows good cyclic stability, the amount of lithium that can be stored is limited by the number of vacant sites in the crystal lattice. Higher storage capacities may be achieved by using conversion type reactions which involve structural reorganization of the crystal lattice during the solid-state redox reaction, however. Such type of reactions were reported originally for nanosized transition metal oxides [1], subsequently various other transition metal compounds MX_n (where X: N, F, S, P and H) have been explored [2–8]. A general reaction scheme is expressed by the following equation:

$$M_mX_n + (n\cdot y)Li^+ + (n\cdot y)e^- \leftrightarrow mM + nLi_yX$$

As this reaction involves the transfer of multiple electrons/lithium ions per formula unit, an increase of the specific capacity of electrode materials may be achieved [9]. Transition metal fluorides were shown to react at high potentials versus lithium and therefore may be suitable candidates for the use as positive electrodes in lithium-ion batteries [3,4]. The high reaction potential was attributed to the highly ionic character of the metal fluoride bond. However, due to the large bandgap, metal fluorides exhibit electrically insulating behaviour as well. This problem can be mitigated by using nanoscale materials and conductive additives such as carbon [3,4].

High specific capacities were reported for carbon metal fluoride nanocomposites produced by ball milling [4,10] but a lack of cyclic stability was prevalent in these materials. This may be attributed to a loss of electrical connection between the current collector and electrode particles during the structural reorganization of the crystal lattice, in addition to volume change of the active material. Thus, new electrode architectures may become necessary in order to maintain not only electric- but also ionic conductivity of the electrode material upon prolonged cycling.

In this context we have developed a synthesis method which is based on the pyrolysis of a mixture of metallocene and LiF, to produce the lithiated state of metal fluoride electrode materials [11,12]. In this process, a mixture of LiF and ferrocene is heated at 700 °C in a closed reaction vessel under inert conditions. The decomposition of ferrocene occurs during pyrolysis and iron nanoparticles are formed which are intimately mixed with LiF in a matrix of graphitic carbon nanostructures. The resulting [Fe/LiF/C] composite has shown a capacity of $230\,mAh\,g^{-1}$ (FeF_3 theoretical specific capacity $712\,mAh\,g^{-1}$) at $20.38\,mA\,g^{-1}$ in a voltage range of 1.3–4.3 V, for over 200 cycles. However, this method has a drawback of concomitant formation of Fe_3C phases which limits the amount

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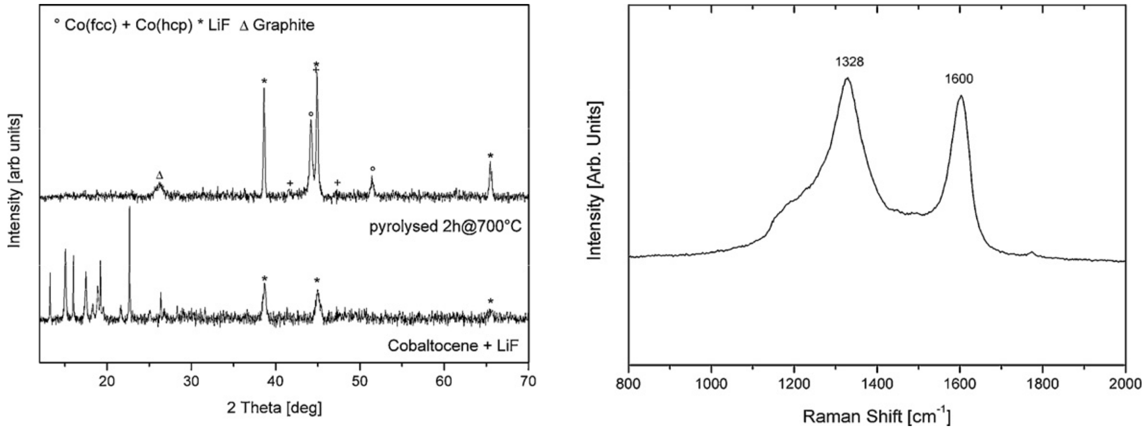

Fig. 1. XRD pattern of ball milled mixture of cobaltocene (unassigned peaks) and LiF as well as [Co/LiF/C] composite (left); Raman spectrum of the [Co/LiF/C] composite (right).

of electrochemically active Fe in the composite [12]. Therefore, synthesis of analogous cobalt composite is intriguing, because carbide formation is less likely to occur in this case. It is the aim of this work to explore the structure and the electrochemical properties of such a composite which is synthesized by the pyrolysis method mentioned above.

Except for one report on a thin film [13], to our knowledge no efforts have been made to synthesize Co/LiF nanocomposites. The studies on preparation of CoF_2 and Co-LiF based electrodes by pulsed laser deposition [13,14] and by ball milling of CoF_2 with carbon [4,10] showed the feasibility of Li extraction from LiF in presence of nanosized Co as well as the reverse reaction, namely formation of Co and LiF by insertion of Li in CoF_2, as it is described by the following equation:

$$CoF_2 + 2Li^+ + 2e^- \leftrightarrow Co + 2LiF$$

Herein we report the synthesis of a [Co/LiF/C] nanocomposite from a mixture of cobaltocene and LiF by pyrolysis under inert conditions. The structure, morphology, and electrochemical properties of the composite are studied and compared with that of the analogous [Fe/LiF/C] nanocomposite and a [CoF_2/C] composite prepared by ball milling.

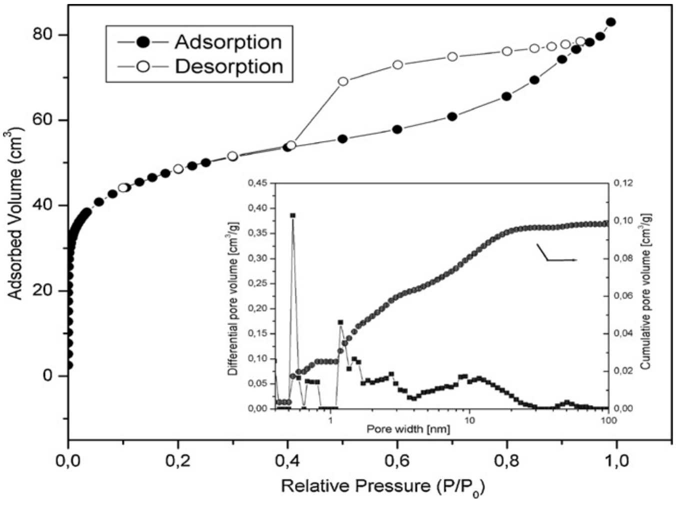

Fig. 2. Adsorption isotherm of [Co/LiF/C] composite at liquid N_2 temperature. Inset: plot of cumulative pore volume and differential pore volume vs. pore width (BET surface area: 177 m^2 g^{-1}; volume of micropores: 0.05 cm^3 g^{-1}; total pore volume: 0.1 cm^3 g^{-1}).

2. Experimental

All experiments were carried out under argon atmosphere using glove boxes and standard Schlenk techniques. Cobaltocene and LiF (Alfa Aesar) were dried under vacuum for 15 h at 40 and 150 °C, respectively. LiF was ball milled in a Fritsch Pulverisette-6 with tungsten carbide balls (1.6 mm) and vial (volume 80 mL) for 20 h at 650 rpm with a ball to powder ratio of 65:1 in pentane without active cooling. The ball milled LiF was mixed with cobaltocene in a molar ratio of 1:3 and homogenized for 5 h at 350 rpm. The mixture (1.2 g) was then loaded into a stainless steel reactor which was closed with Swagelok® VCR fittings. The reactor was placed in a quartz glass tube which was rotated at 10 rpm in a furnace to mix the reactants during the pyrolysis. Pyrolysis was carried out for 2 h at 700 °C. After pyrolysis the reactor was allowed to cool to room temperature naturally. The pressure which developed inside the reactor due to formation of volatile side products was carefully released and the reactor was opened under argon atmosphere.

[CoF_2/C] composites were prepared by ball milling CoF_2 (Alfa Aesar) with 30 wt.% synthetic graphite (Alfa Aesar) for 3 h (WC balls, B/P ratio 190:1, 600 rpm).

Powder X-ray diffraction patterns were recorded with a Bruker D8 Advance Powder Diffractometer (Cu-Kα radiation) using an airtight specimen holder. Raman spectra were obtained using a WiTec CRM200 confocal Raman microscope with an excitation laser at 633 nm (HeNe Laser). Measurements from 10 different spots were accumulated in one spectrum to get averaged information about the carbon structure.

Scanning electron microscopy was performed with a LEO 1530 at 15 keV using carbon tape as substrate. Transmission electron microscopy (TEM) was carried out on an image corrected FEI Titan 80-300 operated at 300 kV in TEM and HAADF-STEM mode, equipped with a Gatan Imaging Filter Tridem 863 and an EDAX s-UTW EDX detector. TEM samples were prepared from dispersion in dry pentane by placing a droplet of the suspension on a carbon grid and allowing it to dry before the measurements. The grids were sealed and reopened just before loading them into the TEM, reducing exposure to atmosphere to about a minute.

Galvanostatic battery tests were carried out at 25 °C with an Arbin battery tester in Swagelok® type cells. The nanocomposite powder was used as cathode material without addition of binders and separated from the anode by Whatman D/F glasfibre separators. Lithium foil (Goodfellow) was used as anode. A 1 M solution of $LiPF_6$ in ethylene carbonate and dimethyl carbonate was used as electrolyte (LP30/Merck). The cathode material was collected at desired states of charge and rinsed with anhydrous DMC. Then the dried samples were analysed by TEM and XRD. Nitrogen-physisorption measurements were conducted with a Micromeritics ASAP 2020 system at 77 K. Prior to measurements the samples were degassed at 350 °C for 12 h in vacuo. Pore size distributions were calculated based on a DFT model [15] assuming slit-shaped pores. The specific surface area was determined according to the BET theory [16].

3. Results and discussion

During the pyrolysis process cobaltocene initially sublimates to form a vapour which subsequently decomposes into cobalt and carbon as the temperature is further increased. Thereby, cobaltocene serves not only as precursor for cobalt nanoparticles but also for the carbon structures. By rotating the reaction vessel, LiF was mixed with the in situ produced cobalt and carbon to form [Co/LiF/C] nanocomposite.