



## Spherical cobalt/cobalt oxide - Carbon composite anodes for enhanced lithium-ion storage



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### ABSTRACT

Herein we report a simple and scalable route to synthesize porous cobalt/cobalt oxide - carbon sphere composites as anode material for rechargeable lithium-ion batteries. It involves the impregnation of starch-derived hydrochar spheres with a cobalt salt, followed by a heat treatment (700 °C) under inert atmosphere. The obtained high surface area (~670 m<sup>2</sup> g<sup>-1</sup>), submicron spheres (~300 nm diameter) with high-degree of microporosity (81%) consist of an amorphous carbon matrix with embedded Co/CoO nanoparticles (~6 nm sized), having a total cobalt content of 6.2 wt%. The hybrid sphere anodes demonstrated superior specific capacity, rate performance and cycling stability. Discharge capacities of 520 and 310 mA h g<sup>-1</sup> are observed at charge-discharge rates of 0.1 and 1C respectively. No significant capacity fading is identified on prolonged cycling at various current densities. The electrode also demonstrated excellent structural stability during extended charge-discharge processes.

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### 1. Introduction

In terms of sustainability issues, carbonaceous materials derived from renewable resources can play an important role in the near future thanks to a myriad of structural, morphological and compositional designed formulations able to solve the evermore pressing problem of current CO<sub>2</sub> emissions via low-tech incorporation procedures of the biomass carbon into advanced materials, long-enduring CO<sub>2</sub> collectors [1,2].

Given the worldwide increasing demand, new materials possessing great performances in energy conversion, storage and usage has become a key task of the scientific community. Rechargeable Li-ion batteries (LIBs) with high energy density, long cycle life and environmental friendliness represent the dominant power sources

for modern industrial and civil portable electronic devices. Due to their higher specific charges and more negative redox potentials than most metal oxides, chalcogenides and polymers, associated with an outstanding stability against harsh environments, small volume change (~10%) during lithiation and tunable porosity, carbonaceous materials are considered as a major material for negative electrode in rechargeable LIBs [3,4]. Although graphite is the choice of anode material with a theoretical capacity of 372 mA h g<sup>-1</sup> (limited due to the formation of LiC<sub>6</sub>) [5,6], it cannot fully meet the needs of high power applications (e.g. hybrid electric and electric vehicles, power tools, the back-up for wind and solar energies, and so on) [7,8].

In this context, two forefront research directions emerge: the development of alternative carbonaceous materials and alternative anodes to the carbonaceous materials [9–11]. The first imply mainly the manipulation of carbonaceous materials structure, morphology, porosity (from microporosity to hierarchical three-dimensional macroporosity), modification of their chemistry with non-carbon elements such as nitrogen and boron [9,12–16].

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Although none of the approaches is drawback-free, generally (i) amorphous and turbostratic carbon rather than graphitic carbon provide a better Li-ion storage capacity, suggesting that there are means other than intercalation for Li-ions accommodation [17]; (ii) the spherical morphology is helpful for the electrochemical performance allowing an uniform current distribution that induces a reduced decomposition of the electrolyte and avoiding dendrite formation, being also advantageous as regards packing density, structural stability, surface to volume ratio [17–19]; (iii) the porosity including pore connectivity impose the electrochemical performing, ruling the Li-ions interfacial diffusion kinetics, electrode–electrolyte contact area [20–22].

Among the contenders to carbon anode materials are transition metal oxides (CoO, Co<sub>3</sub>O<sub>4</sub>, NiO, Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, SnO<sub>2</sub>, etc) characterized by high electrochemical capacity of commonly over 700 mA h g<sup>-1</sup>, due to the so-called conversion reaction mechanism [23–26]. But their large specific volume change during lithiation/delithiation reactions induces a loss of physical integrity by disintegration and a severe deterioration of nanometric nature by aggregation, leading to a gradual decay of reversible capacities during extended C/D cycles [27,28]. To circumvent these shortcomings, different approaches were developed, among which: (i) the design of proper architectures of downsized particles such as nanowire [29,30], nanorods [31,32], nanobelts [33] nanocages [34,35], hollow structures including nanotubes [36–39], etc., with tailored porosities [40,41] that are expected to mitigate the physical strains thanks to the ability to accommodate large volume changes; (ii) the addition into the oxide electrode material of small quantities of an inert but conducting metallic component that promotes/activates the reversible transformation of some solid electrolyte interface (SEI) components leading to improved capacity retention upon cycling [42–44] and (iii) the integration into the active metal oxide nanomaterials of a carbonaceous matrix that can act both as structural buffer and conductive agent, accommodating the mechanical strains during the lithiation/delithiation process while inhibiting agglomeration, and enhancing the electrical conductivity [45,46].

Herein, the chosen strategy for building a LIBs anode is somehow inverse to the last aforementioned one: instead of carbon based material incorporation into the metal oxide we doped the carbonaceous materials with transition metal ions. Such scheme makes possible the improvement of carbon materials electrochemical properties by introducing small amounts of metal (~6 wt %), while capitalizing the diversity of carbon preparative chemistry both in terms of the carbon source and synthesis methodology. Note that the metal content in the already reported integrated metal oxides-carbonaceous anodes is much higher, for example the cobalt content derived from different cobalt oxides is higher than 20% [47–49]. The utilized synthetic approach is facile and scalable, involving a hydrothermal carbonization procedure under mild conditions (180 °C, P < 10 barr) of a carbohydrate or biomass for the synthesis of semicarbonized functional materials (hydrothermal carbons or hydrochar), an impregnation procedure as metal deposition technique followed by a thermal carbonization under argon atmosphere of the metal containing hydrochar. A special mention for the method versatility that can be developed on each level of the procedure: (i) assortment of the natural carbon sources, from biomass to its constituent carbohydrates (either mono, di- or polysaccharides) [1,50–52], (ii) uncomplicated size and shape tailoring of the hydrothermal carbons *via* a convenient variation of the carbon source and/or synthesis parameters [53,54], (iii) a large variety of metal dopants and doping concentrations by means of a simple selection of the metal salts (the single limitation is their water solubility) and adjustment of their concentration and (iv) a straightforward manipulation of both carbonaceous material

porosity (from the lack of porosity to high micro- or relatively important mesoporosity) and graphitization degree, by an appropriate thermal processing and/or by introduction into the carbonaceous matrix of small amount of graphitization metals [55–57].

The present study presents an electrochemical assessment of a metal doped carbonaceous material as anode materials for lithium ion batteries, that brings together a clear-cut, high yield and low cost synthetic methodology and the benefits of a disordered carbon structure with microporous spherical morphology generated from starch (the second most abundant biopolymer after cellulose), of small amounts of CoO electrochemically active metal oxide (theoretical specific capacity of 716 mA h g<sup>-1</sup>) [58,59] and metallic cobalt as conductive metal. All these material's features fasten into a hybrid microstructure are accountable for the superior electrochemical performances as anode material for rechargeable Li-ion batteries.

## 2. Experimental

### 2.1. Materials

Commercial soluble starch (Carl Roth GmbH, 11.20% water content determined by thermal analysis) and cobalt acetate tetrahydrate Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (Reactivul) of analytical grade were used as received without further purification.

### 2.2. Synthesis

The cobalt containing porous carbon spheres (CoPCSs) were obtained by a simple procedure implying hydrochar spheres (CS) synthesis *via* hydrothermal carbonization (HTC) of starch [60], cobalt cations incorporation on the as-prepared spheres by an impregnation method, and a post-synthesis annealing treatment in inert atmosphere (argon). The following reaction conditions were used for here considered CoPCSs: (i) a hydrothermal reaction at 180 °C for 24 h using a 0.3 M starch aqueous solution, the resulted black products being collected by centrifugation, washed with double distilled water and ethanol several times and dried at 60 °C for 5 h; (ii) the cobalt cations were deposited on carbonaceous surface by an impregnation: the as-prepared starch-derived carbonaceous spheres were uniformly dispersed in 100 ml double distilled water by ultrasonication (15 min) and mixed with a solution of 130 ml double distilled water containing Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (weight ratio Co<sup>2+</sup>/CS = 9), subsequently magnetically stirred 4 h and aged 48 h at ambient temperature; the cobalt-coated hydrochar spheres (CoCSs) were gathered by centrifugation, washed with double distilled water and ethanol several times and dried in vacuum at 80 °C for 6 h; (iii) a calcination in argon dynamic atmosphere at 700 °C for 3 h, with a heating rate of 10 °C min<sup>-1</sup>. The as-obtained argon treated composites contain 6.2 wt % Co, determined by air-atmosphere thermal analysis up to 1000 °C, the final solid residue being CoO (values averaged from at least three experiments) and confirmed by EDX measurements taken on different large areas including at least 50 spheres.

### 2.3. Characterization

Fourier transform infrared spectroscopy (FTIR) was performed with a Bruker Tensor V-37 FTIR spectrophotometer. Thermal measurements were performed with a Netzch STA 449 F1 Jupiter simultaneous thermal analyzer at a heating rate of 5 °C min<sup>-1</sup>, in inert (argon) dynamic atmosphere. X-ray diffraction measurements were carried out at room temperature on a PANalytical X'Pert PRO MPD X-ray diffractometer with a Cu X-ray tube providing a K<sub>α</sub> wavelength of 1.5418 Å. Raman spectra were recorded by Horiba

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