

Electro-Spun Self-Standing CoO_x/C/Graphene Mats as Binder-Free Anodes for Flexible Li-ion Batteries: Performances and Perspectives

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Abstract Self-standing cobalt-oxide/carbon/graphene (CoO_x/C/G) fibrous mats are synthesised by electro-spinning (ES). Mats are characterised by complementary techniques and tested as binder-free anodes for flexible Li-ion batteries (LIBs). Their electrochemical performance is compared with that of the corresponding electro-spun Co₃O₄ powders, and perspectives for the material improvement are discussed.

Introduction

The increasing demand for wearable or aesthetically-appealing electronics has led to the inclusion of flexibility among the basic requirements which LIBs have to possess besides lightweight, large capacity, high rate capability and cyclic stability. Low electronic conductivity and poor transport properties of the common electrode materials (e.g. Co₃O₄ [1,2]) have encouraged the use of C additives, and particularly of G [2]. This work deals with the synthesis of CoO_x/C/G mats by ES, a very commercially competitive technique thanks to its simplicity, cheapness, versatility and scalability [3,4].

Experimental

Pure Co₃O₄ powders or self-standing flexible CoO_x/C/G mats can be obtained by proper thermal treatments of the fibres, spun by using Co acetate, polyacrylonitrile, N,N-dimethylformamide and graphene-oxide as Co-oxide precursor, polymer, solvent and C-additive (if any), respectively.

Morphology and surface composition of the samples and crystalline phase of the oxide were investigated by means of scanning and transmission electron microscopy (SEM and TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and micro-Raman spectroscopy (MRS).

Performances of the samples as anodes were evaluated via half-cell tests using a lithium foil as the counter electrode, 1M LiPF₆ in EC+PC+DMC 1:1:1 v/v as the electrolyte, and glass fibres as the separator. Coin cells were assembled in a high-purity argon-filled glove box. Preparation of the working electrode required no addition of chemicals to the CoO_x/C/G mats, while Super P carbon black and PvdF in a weight ratio of 2:1:7 were added to the Co₃O₄ powders. The galvanostatic charge/discharge characteristics were recorded at room temperature with a VMP3 electrochemical workstation.

Results and Discussion

Morphology and surface composition of the samples and crystalline phase of the oxide. Owing to thermal degradation of the polymer, powders consisting of very short fibres (Fig.1a) are obtained by oxidation in air at 600°C of the as-spun film. Instead, stabilisation in air at lower temperature (225°C), followed by carbonisation at 600°C in inert atmosphere, preserves the carbonaceous film component and leads to flexible mats consisting of smoother and thinner fibres (Figs.1b–c). TEM reveals that oxide nanoparticles (NPs) are embedded in the carbonaceous fibre matrix (Fig.1c), in line with results obtained, via the ES technique, by other authors [1,4].

XRD, MRS (Fig.1d) and XPS (Fig.1e) analyses indicate that only Co₃O₄ is formed in the case of powders, while in the other case, regardless of the carbonisation ambient (helium or vacuum), two different oxide phases (Co₃O₄ and CoO) are obtained because of the carbo-thermal reduction of the fibre surface during the carbonisation upon inert atmosphere in the presence of carbon [5], leading to CoO_x/C/G fibres,

with Co_3O_4 and CoO NPs respectively located in the core and the outer shell of the fibres.

Electrochemical Performances and Perspectives. As shown in Fig. 2a, the anode consisting of pure Co_3O_4 powders (with binder) exhibits higher initial specific capacity (1580 mA h/g) but very poor stability (it undergoes a 75% reduction at the 5th cycle); conversely, in spite of the lower initial capacity (990 mA h/g), the anode realised with the $\text{CoO}_x/\text{C}/\text{G}$ mats fibrous mat without the addition of any chemicals appears to be by far more stable. After 75 cycles at a 100 mA/g current density (Fig. 2b), it still retains a specific capacity higher than that of graphite (455 against 372 mA h/g) and a coulombic efficiency of 100% (inset of Fig. 2b).

The specific capacity after 5 cycles (590 mA h/g) is higher than that theoretically expected (505 mA h/g) on the basis of the material composition (~75 wt% of carbon) inferred from the XPS analysis. This hints at the occurrence of synergistic effects among the three fibre components (carbon, graphene, and CoO_x). Interestingly, by applying the same calculation to the data reported for electro-spun $\text{Fe}_2\text{O}_3/\text{C}$ fibres [4], a comparable ratio (1.17) between the measured value and the theoretically-expected one is obtained, which might indicate the existence of any limitation intrinsically related to the morphology obtainable by the ES technique.

Indeed, the absence, in the charge curves (Fig. 2a), of the plateaux typical of the oxides suggests that CoO_x NPs embedded in the carbonaceous matrix are not very active after few cycles, in agreement with literature [1,4]. Regardless of their morphology, only oxides whose surface is largely accessible (rather than being partly embedded in the carbon matrix) continue to contribute after few cycles [2,5]. On the other hand, the carbon matrix, besides favouring charge transport, provides the composites with the needed flexibility. Hence, future work will be aimed at improving the performance of the electro-spun composites through various strategies, i.e. taking action on the carbonaceous component of the fibre, on the composite-fibre surface, as well as on the spinning geometry.

Acknowledgements

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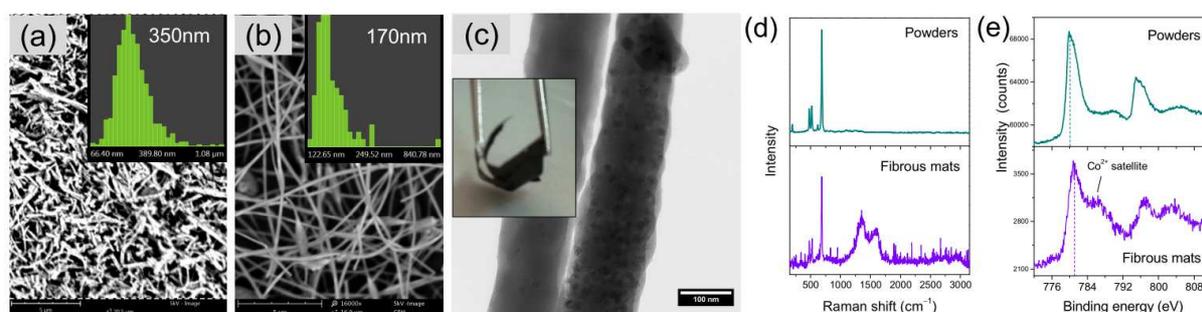


Fig.1 (a–b) SEM and (c) TEM images of (a) CoO_x powders and (b–c) $\text{CoO}_x/\text{C}/\text{G}$ fibres; (d) MRS and (e) XPS spectra.

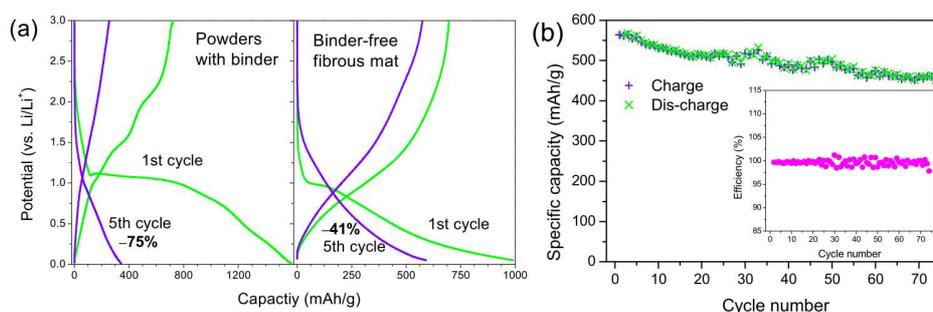


Fig.2 (a) Charge/discharge curves of the investigated samples (current density: 100 mA/g); (b) cycling stability of the $\text{CoO}_x/\text{C}/\text{G}$ fibres (inset: coulombic efficiency).