

Nanotechnology for the progress of lithium batteries R&D

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Abstract

In this paper we report the strategy followed in our laboratories for the progress of lithium ion batteries. The results show that nanotechnology is a very promising tool for achieving breakthrough in electrode and electrolyte materials. The concept is demonstrated for the cases of metal storage and metal oxide anodes, phospho olivine lithium iron phosphate cathodes and solvent-free, poly(ethylene oxide)-based polymer electrolytes.

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Keywords: Nanotechnology; Lithium batteries; Anodes; Cathodes; Electrolytes

1. Introduction

Today lithium-ion batteries are the power sources of choice for popular portable electronics, such as cellular phones and note books [1]. However, despite their outstanding commercial success, these batteries are still open to improvements. Indeed, the chemistry of lithium-ion batteries has not changed since their introduction in the market in the early nineties. Basically, the batteries use a graphite anode, a lithium cobalt oxide, LiCoO_2 (or, occasionally a lithium manganese spinel, LiMn_2O_4) cathode and a lithium ion conducting electrolyte, e.g. a solution of LiPF_6 in an ethylene carbonate–dimethylcarbonate, EC–DMC, organic solution mixture [2]. Although widely used, this is not necessarily the best cell combination and indeed, improvements in energy and power content are requested to meet the increasing user's demands.

Nanotechnology is the best tool for achieving breakthroughs in lithium battery electrode and electrolyte materials. In this paper we review the investigations and the results carried out in our laboratories with the aim of developing advanced lithium batteries based on nanomaterials.

2. Anode materials

As already mentioned, graphite is the most common anode material used in commercially established lithium bat-

teries. Graphite has a good cycling stability but a relatively low specific capacity, i.e. not exceeding 372 mAh g^{-1} . Thus, if improvement in energy content is desired, new, high capacity alternative electrode materials have to be developed. In this respect, lithium storage metals appears as very appealing candidates. A number of metals, e.g. Al, Si, Sn, . . . , are capable of reacting with lithium to reversibly form intermetallic, lithium alloys compounds.

These alloys are in principle almost ideal anodes for lithium batteries: they can store and release large amount of lithium, assure high voltages when combined with lithium metal oxide cathodes and provide values of specific capacity exceeding that of graphite by an order of magnitude [3]. Examples are given in Table 1 [4].

Unfortunately, the accommodation of the large amount of lithium is accompanied by severe volume changes in the host metal. These in turn induce mechanical strains which lead the electrode to crack and, eventually disintegrate with its failure in the round of few cycles. An effective way to improve the cycling stability of the metal alloy electrodes is that of modifying their morphology by reducing their particle size to few nanometers or by designing special nanostructures.

Indeed, this strategy is expected to have a two-fold effect on the performance of the electrodes—(i) improvement in cycling stability, since small particles enable to more easily accommodate the mechanical strains (the absolute volume changes are smaller than for larger particles, although the relative changes are the same) and (ii) enhancement of power due to the reduction of the lithium ion diffusion length. The validity of this strategy has been confirmed by various

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Table 1
Theoretical specific capacity for selected lithium storage metals and for graphite

Unlithiated metal	Fully lithiated metal	Gravimetric capacity (mAh g ⁻¹)	Volumetric capacity (mAh cc ⁻¹)
Al	LiAl	993	1.374
Si	Li ₂₁ Si ₅	4008	2.323
Sn	Li ₂₂ Sn ₅	994	2.025
Sb	Li ₃ Sb	660	1.881
C, graphite	LiC ₆	372	0.760

authors [5–7]. An example of metal storage electrode nanostructure is shown in Fig. 1 which refers to a silicon electrode prepared with a nano pillar surface morphology [8]. Tests run in a lithium cell demonstrated that a considerable improvement in cycling response is indeed obtained with this nanostructured electrode [8].

Nanostructures are also highly beneficial for other classes of alternative electrode materials, e.g. for metal oxide electrodes. For instance, it is known that tin oxide can electrochemically react with lithium with a first process involving the formation of lithium oxide and tin, followed by a Li–Sn alloying–dealloying reversible process [9]. It is assumed that the “in situ” formed lithium oxide can act as a “buffer” for

accommodating the volume changes which accompany the second alloying process [10]. However, if common electrode morphologies are used, the cycling stability of the tin oxide electrode is still unsatisfactory [11].

Considerable improvements are obtained when passing to nanostructures. Fig. 2 shows the morphology of tin oxide prepared in form of nanofibrils using a specific template technique [12]. Tests in a lithium cell demonstrate the high cycling stability and especially, the high power characteristics of these, advanced, nanostructured tin oxide electrodes.

3. Cathode materials

Improvements at the cathode side are also critical for the progress of lithium batteries. Indeed, considerable efforts are presently directed to the replacement of the high cost, partially toxic LiCoO₂ with more affordable and sustainable materials. Promising candidates are iron phosphates, such as the phospho olivine LiFePO₄ which, in a lithium cell, may be reversibly delithiated to FePO₄ [13]. This material is an appealing cathode for lithium batteries: it is cheap, environmentally benign and it has a reasonably high capacity, i.e. approaching that of LiCoO₂ (170 mAh g⁻¹ versus 220 mAh g⁻¹).

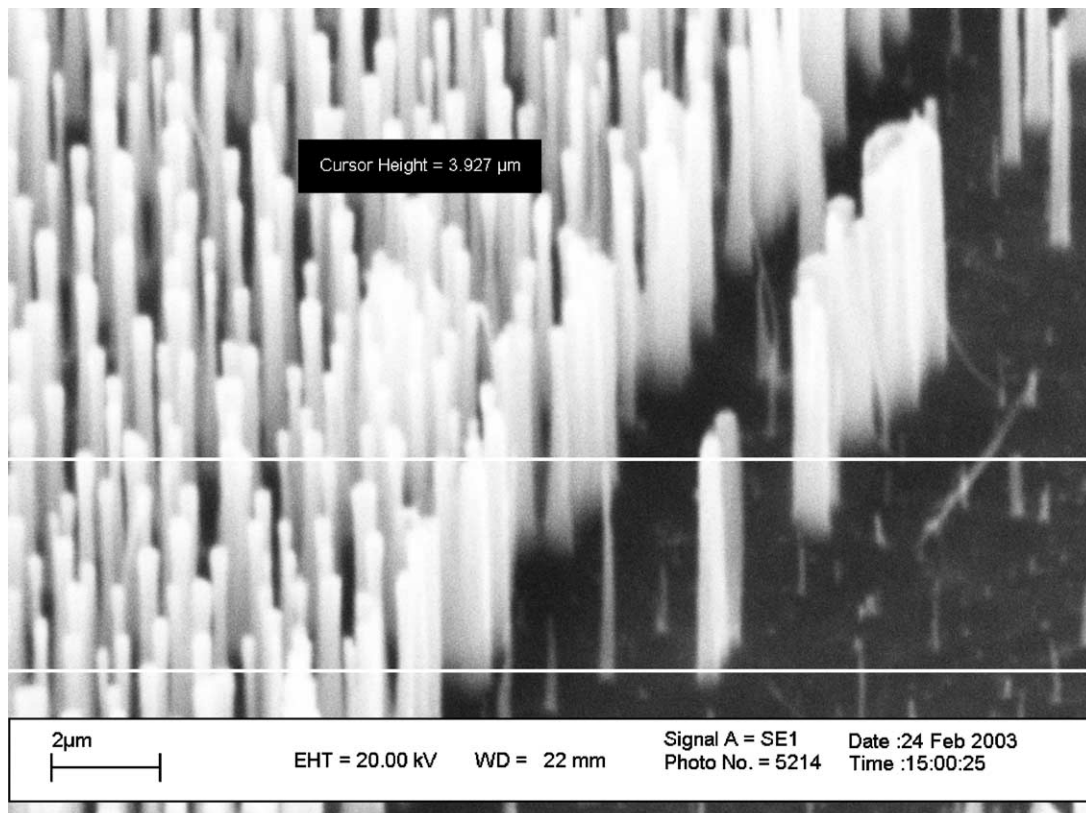


Fig. 1. SEM image of a silicon electrode having a nano pillar surface morphology. Courtesy of Professor Mino Green, Imperial College, London.

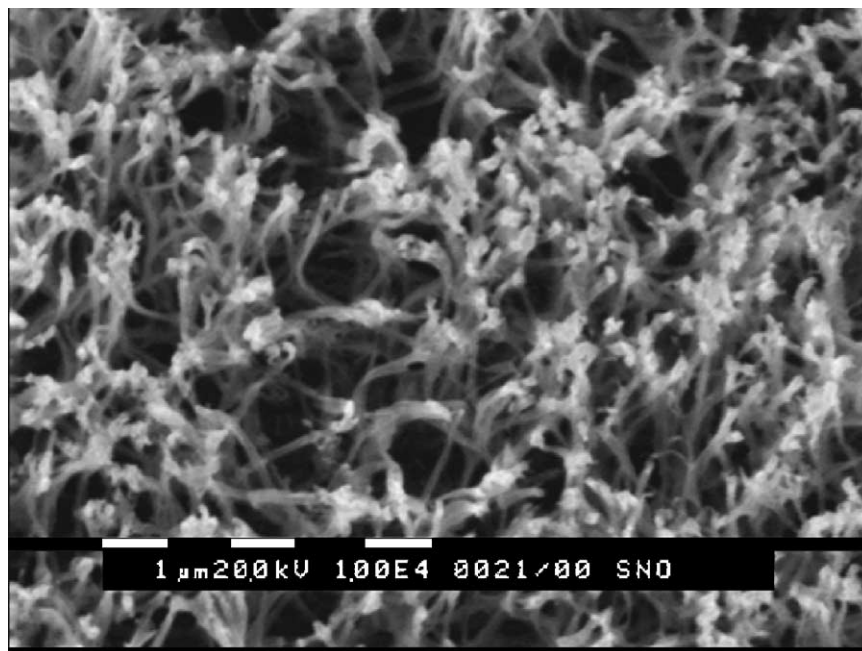


Fig. 2. SEM image of a tin oxide electrode having a nano fibril morphology [12].

However, the kinetics of this electrode are controlled by its poor electronic conductivity and by the low lithium ion diffusion across the reaction phases. Morphological modification at the nano scale level appears the proper tool to control these undesired phenomena. Recent literature work has shown that strategies such as carbon nano-painting [14], nano-fibril textures [15] and carbon nano-dispersion [16] led to excellent improvements in the utilization of the “per se” insulating LiFePO_4 . In this scenario, we have demonstrated that dispersion in the course of the synthesis of metal (e.g. Cu or Ag) powders at the nano particle size, produces LiFePO_4 electrodes with enhanced electrochemical properties [17]. It is believed that the nano powders act as nucleation sites for the growth of the LiFePO_4 particles, as well as conducting bridges between them, this finally resulting in an improvement of the infra- and inter-conductivity of the particles. Indeed, tests in lithium cells have demonstrated that these metal composite LiFePO_4 electrodes can cycle with good capacity delivery at room temperature and at high rates, Fig. 3.

Another strategy for enhancing the performance of LiFePO_4 electrodes is that of preparing them in suitable nanostructures. Fig. 4 illustrates the morphology of a LiFePO_4 electrode prepared in form of nanofibrils following a procedure similar to that used for the preparation of nanostructured tin oxide electrodes, see Fig. 2.

It is expected that the lithium diffusion length is greatly reduced in the nanofibrils, this allowing fast kinetics and good utilization rates. Fig. 5 shows the cyclic response of this morphologically modified LiFePO_4 electrode in a lithium cell using a EC–DMC (1:1)– LiClO_4 1 M liquid electrolyte. It may be seen that high discharge capacity and cyclability

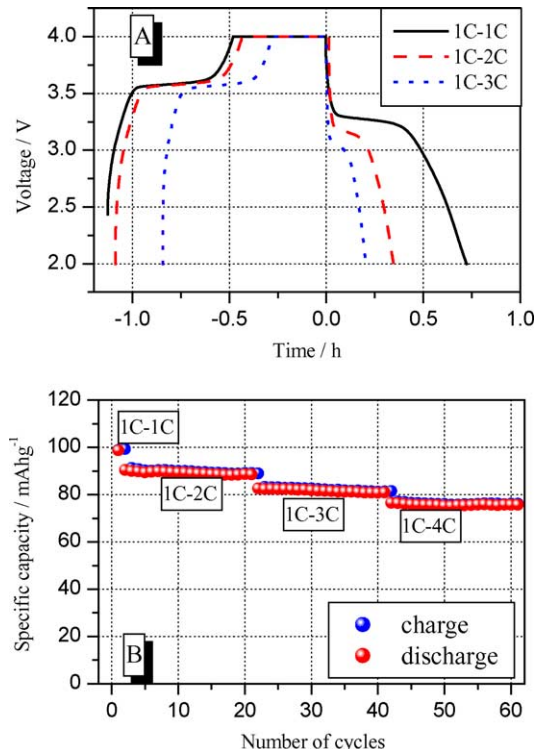


Fig. 3. Galvanostatic charge-discharge cycles of a Ag-composite LiFePO_4 electrode in a lithium polymer cell at room temperature. (A) Voltage profiles; (B) capacity vs. cycle number. Electrolyte: EC–PC– LiPF_6 –PVDF gel. Electrode composition, 83% active material; 12% Super P; 5% PVDF binder.

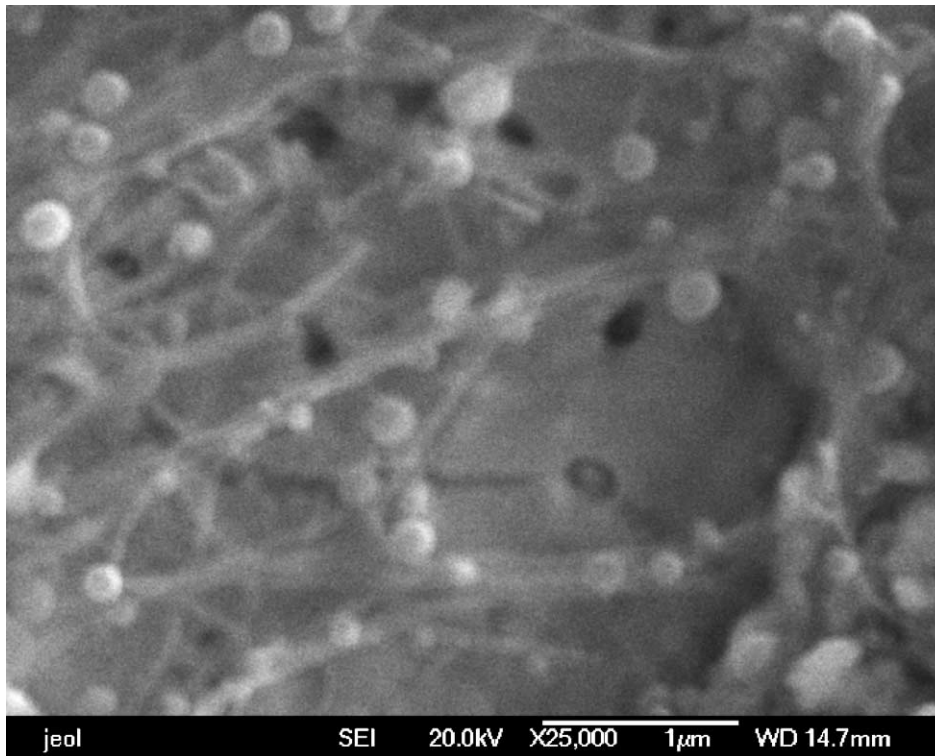


Fig. 4. Nano-fibril morphology of a LiFePO_4 electrode.

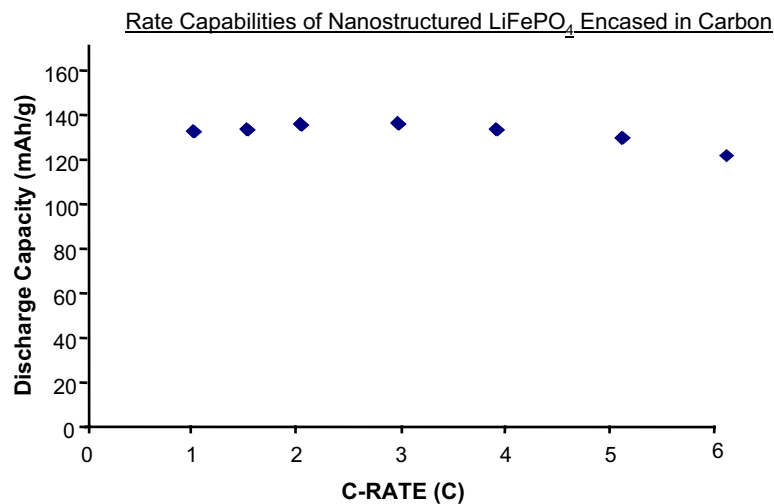


Fig. 5. Discharge capacity of a nano-fibril LiFePO_4 electrode encased in a carbon matrix in a lithium cell at different rates. Electrolyte: EC–DMC (1:1)– LiClO_4 1 M.

are delivered at high rates, even in a polymer electrolyte cell.

4. Electrolyte

In addition to anode and cathode materials, also electrolyte materials play a key role for the progress of lithium batteries. In this respect, particularly welcome would be the replacement of the common liquid electrolyte with a poly-

mer electrolyte, so that to allow the development of reliable and safe innovative cell structures. The most desirable polymer electrolytes are solvent-free membranes, e.g. those based on blends of poly(ethylene oxide) and a lithium salt, PEO–LiX.

However, these electrolytes suffer of a poor ionic conductivity at ambient temperature. We have shown that a promising strategy to improve the transport characteristics consists in dispersing ceramic powders at nano particle size to the PEO–LiX matrix [18]. Indeed, direct experimental

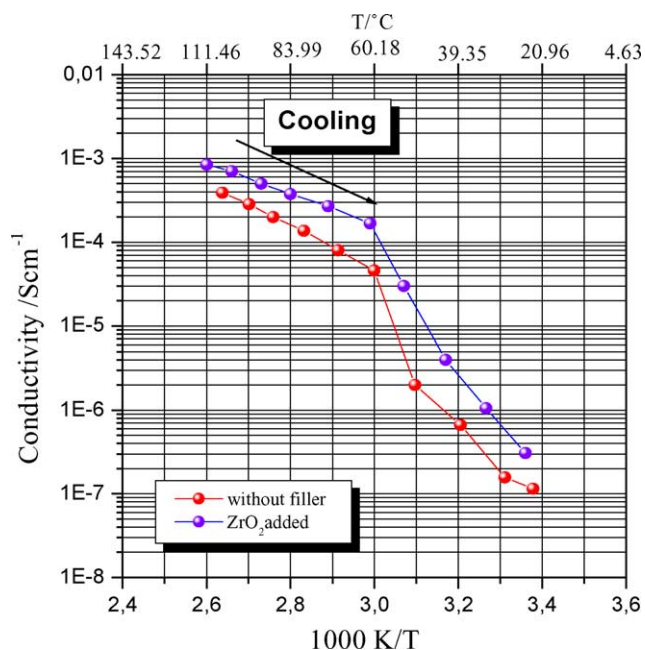


Fig. 6. Arrhenius plot of a P(EO)₂₀LiCF₃SO₃ + 10 (w/o) ZrO₂ nanocomposite polymer electrolyte.

results obtained in our [19,20] and other [21–23] laboratories have evidenced that the nano-dispersion increases several fold the conductivity of the electrolyte. As an example of recent data in this area, Fig. 6 shows the Arrhenius plot of a nanocomposite electrolyte formed by dispersing zirconia powders in the (PEO)₂₀LiCF₃SO₃ matrix [24] compared to that of the plain polymer. It can be clearly noticed a significant enhancement of the composite sample conductivity both above and below 60 °C (the PEO crystallization temperature). This behavior, together with other enhanced important properties, as the cation transference number, the metallic lithium/polymer electrolyte interface stability and a lower degree of the chains crystallinity even at temperatures below the PEO melting point, clearly point to extended interactions between the ionic and molecular components of the polymeric electrolyte and the filler powders, as discussed in details in reference [24].

5. Conclusion

The results described in this work show that nanotechnology may play an important role for the progress of lithium batteries. With suitable morphology modifications, electrode and electrolyte materials which so far have been considered still inadequate may assume a crucial importance for allowing innovative and powerful cell structures. For instance, preparation in suitable nanostructures may confer to metal storage and metal oxide electrodes that level of cycling stability that have so far hinder their use as high capacity anodes. Similarly, morphological changes, as the addition of

nano metal particles, may result in the formation of conduction bridges which allow high capacity utilization and high rates for the low cost and environmentally benign iron phosphate cathodes. Finally, the dispersion of nanoceramic powders enhances the conductivity of solvent-free polymer electrolytes, this removing a drawback which has penalized their use over several years.

Acknowledgements

The authors wish to thank Professor Charles Martin of the University of Florida for the great hospitality, the economical support and the invaluable scientific discussions which was given to FC during his stage at the University of Florida and Professor Mino Green of Imperial College in London, for kindly providing the SEM picture of the nano-pillar silicon electrode.

The financial support of the Italian Ministry for University and Research, MIUR, project COFIN 2002 Nanostructured electrode and electrolyte materials for advanced lithium batteries is also acknowledged.

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