

Recent trends in research activity on lithium-ion batteries in Italy

Catia Arbizzani, Mariachiara Lazzari, Marina Mastragostino*

*University of Bologna, Unità Complessa di Istituti di Scienze Chimiche, Radiochimiche e Metallurgiche,
via San Donato 15, 40127 Bologna, Italy*

Available online 25 May 2005

Abstract

With the aim to give a view of the present research activity in Italy on lithium-ion batteries, the contribution of six Academic groups involved in a National Project “Electrode and Electrolyte Nanostructured Materials for Advanced Lithium Batteries”, which is exploratory in nature for the search of novel or improved materials, also by optimizing materials processing techniques, is here presented and discussed.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Lithium-ion batteries; Nanostructured electrode materials; Graphite-metal composites; Metal alloys; Phosphides; Silicides; Lithium-iron phosphates

1. Introduction

In Italy the research on lithium batteries has been active since two decades and several projects involving Universities, the National Council of Research (CNR), the ENEA government energy agency and the Arcotronics Italia SpA Company have been carried out in the past with successful results [1,2].

With the aim to give a view of the present research activity in Italy on lithium-ion batteries, the contribution of the Universities of Bologna, Camerino, Chieti, Rome “La Sapienza”, Sassari and Torino Politecnico in a National Project in progress (2003–2004) “Electrode and Electrolyte Nanostructured Materials for Advanced Lithium Batteries”, funded by Ministry of Education, University and Research (MIUR), is presented here. The tasks of this project, which is exploratory in nature, are to search for novel or improved materials, to optimize materials processing techniques, to characterize the materials in terms of their structural and morphological properties and to focus on the relationship between physical–chemical properties and electrochemical performance of the developed materials. The strategy of this project is the morphological conversion towards nanostructured materials, with the goal to find improved materials in terms of capacity delivery, cycle life, environmental compatibility and cost.

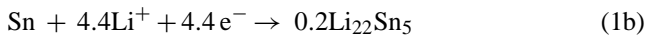
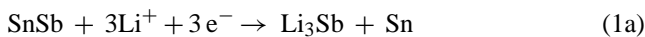
Our studies have been focused on several classes of anode and cathode materials such as ameliorated graphite with nanosized metals, intermetallic alloys, magnesium silicides and metal phosphides as anode materials, and on iron phosphates and mesoporous structures with transition metals as cathode materials. Several synthesis methods have been pursued to prepare nanostructured phases of these materials such as mechanical milling (MM), mechanical alloying (MA), self-sustaining high temperature synthesis (SHS), mechanically activated self-sustaining high-temperature synthesis (MASHS), electro deposition (ED), chemical precipitation (CPR), sol–gel routes (SGR) and template methods (TM).

Structural and morphological characterizations of the synthesized electrode materials were performed by X-ray diffraction (XRD), scanning electron microscopy (SEM), field-emission SEM (FE-SEM) and transmission electron microscopy (TEM), and electrochemical investigations were carried out in T-shaped three-electrode cells with Li in excess as counter electrode and Li as reference, and several combinations of lithium salts and organic solvents as electrolytes.

Graphite is the most used anode materials in lithium-ion batteries for its relatively high capacity and the almost flat charge–discharge voltage profiles. However, one of its major drawbacks is the poor performance at low temperature due to the low diffusivity of lithium [3]. For this reason, a study on ameliorated graphite doped with nanosize metal powders has been carried out in this Project [4].

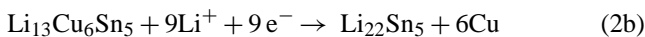
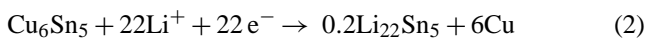
* Corresponding author. Tel.: +39 0512099798; fax: +39 0512099365.
E-mail address: mastrag@ciam.unibo.it (M. Mastragostino).

The approach, after Besenhard and coworkers [5] of the intermetallic alloy's use for storing lithium with controlled volume stress, was pursued by investigating two classes of intermetallics, SnSb and Cu_6Sn_5 alloys. The SnSb lithiation is a two-step process: first, antimony alloys lithium to form Li_3Sb with displacement of tin from the intermetallic compound (the nominal capacity at the end of these step is 334 mAh g^{-1} of unlithiated material (UM)), then, at lower potentials, tin alloys with lithium, via various intermediate Li_xSn phases, to a maximum Li/Sn atomic ratio of 4.4 (the total nominal capacitance at the end of this step is 825 mAh g^{-1} UM) according to equations below, which are the total lithiation reaction (Eq. (1)) and the partial lithiation reactions (Eqs. (1a) and (1b)):



The intermetallic SnSb was investigated with particular emphasis on the optimization of its morphology to improve cycle-life at high delivered specific capacity, and also a lithiated intermetallic alloy ($\text{Li}_4\text{Sn}_{0.72}\text{Sb}_{0.28}$) was synthesized and tested with the aim to further limit the volume stress and improve cycle-life [6].

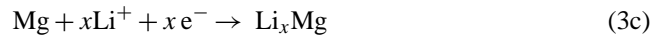
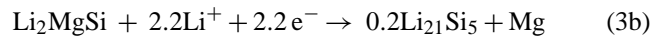
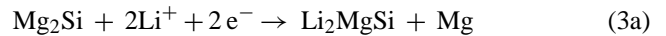
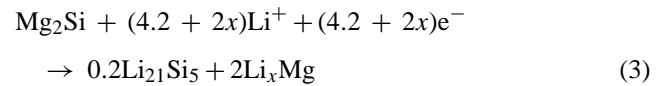
The Cu_6Sn_5 alloy, in which Cu is a non-reacting component toward lithium with the role to “buffer” the volume changes during tin alloying with lithium, can store up to a Li/Sn atomic ratio of 4.4 with a nominal specific capacity of 605 mAh g^{-1} UM. However, the Cu_6Sn_5 shows structural compatibility only with its lithiated phase $\text{Li}_x\text{Cu}_6\text{Sn}_5$ ($0 < x < 13$) [7], so that the sublattice of Sn, which is the active component of the intermetallic compound, suffers moderate distortion in the lithiated phase only up to a Li/Sn atomic ratio of 2.6, displaying a nominal specific capacity of 358 mAh g^{-1} UM according to the equations below displaying the total lithiation reaction (Eq. (2)) and the partial lithiation reactions (Eqs. (2a) and (2b)):



To enhance cycle-life of Cu_6Sn_5 much attention has been focused on a new three-dimensional substrate, carbon paper, able to host or to be homogeneously covered by micrometric aggregates of nanometric Cu_6Sn_5 and to function as current collector [8].

Also metal silicide alloys have been thought as anode materials for lithium-ion batteries given the Si good affinity to Li and the ease of Li insertion into their structures. Among metal silicides, Mg_2Si and $\text{Li}_4\text{Mg}_2\text{Si}$ were investigated in the Project [6]. The lithium insertion process in the Mg_2Si of Eq. (3) involves several steps. When Li is intercalated to form Li_2MgSi and segregate Mg its nominal specific capacity is 1023 mAh g^{-1} UM; beyond this insertion limit, the ternary

compound decomposes into binary Li_xSi alloys up to $\text{Li}_{21}\text{Si}_5$ and Mg; also Mg which is formed during the partial lithiation processes described in Eqs. (3a) and (3b) has certain solubility for Li, as indicated in Eq. (3c):



Some transition metal phosphides such as MnP_4 , CoP_3 , FeP_4 and CuP_2 have been recently investigated as anode for lithium-ion batteries [9–12] and the NiP_2 , a new anode material, is under investigation in our Project, and LiP, too, is under study [13].

Improvements at the cathode side are also important to ameliorate lithium-ion battery performance. The efforts directed to the replacement of LiCoO_2 with cheaper and environmental compatible materials indicated that iron phosphate and lithium iron phosphate may be promising candidates, taking also into account their nominal capacity of 178 mAh g^{-1} of UM or 170 of lithiated material, reasonably near that of LiCoO_2 , according to Eq. (4).



However, the poor electronic conductivity and the low lithium ion diffusion across the reaction phases of this electrode requires that FePO_4 or LiFePO_4 are modified by adding of conducting agents and from the morphological point of view to reduce the diffusion path length. Along this line $\text{RuO}_2\text{-FePO}_4$ composites [14] and carbon covered LiFePO_4 have been prepared via sol-gel routes [15], starting from cheap Fe(III) salts, and LiFePO_4 nanotubes covered by carbon have also been prepared by a innovative template synthesis [16]. Also mesoporous Si-based materials containing ions of suitable transition metals, prepared by template methods, are under investigation.

In addition to anode and cathode materials, also electrolyte materials play an important role for advanced lithium batteries. In this respect, the replacement of common organic electrolytes with polymer electrolytes would be welcome, particularly for safe innovative cell designs. In this Project also new solvent-free PEO-based electrolytes have been investigated [17,18].

2. Results and discussions

Advanced carbonaceous materials, i.e. nanosized metal-graphite composites have been developed at Camerino and Chieti Universities from a simple preparation route. Graphite, which was oxidized by chemical “wet” or thermal “dry” procedure was added to nanosized “doping” powders obtained

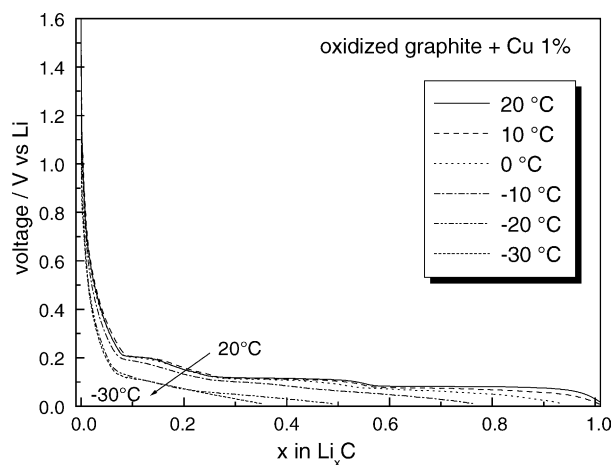


Fig. 1. Voltage profiles at different temperatures of oxidized graphite-1 wt.% Cu composite electrode at C/5 (courtesy of Professor Roberto Marassi, Camerino University).

by mechanical stirring of carbon and metal (Ag, Cu, Au and Ni). By mechanical stirring of oxidized graphite 84.5 wt.%, nanosized “doping” powder 5 wt.%, polyvinylidene fluoride (PVDF) 10 wt.% and $\text{H}_2\text{C}_2\text{O}_4$ 0.5 wt.%, a slurry in *N*-methyl-2-pyrrolidone (NMP) was yielded and the electrodes, prepared on Cu current collectors using a doctor blade technique, were tested in ethylene carbonate: diethylene carbonate: dimethyl carbonate (EC:DEC:DMC)-1 M LiPF_6 . The intercalation curves of the different composites at different temperatures showed that the composite with nanosized Cu is the most effective in improving the electrode performance at low temperatures. Fig. 1 displays the curves of Cu-graphite which retains the 40% of its intercalation capacity at -30°C , a relevant result for lithium battery use at low temperatures [4].

Mixtures of the two phases Sn and SnSb with nanosized particles were obtained at Roma “La Sapienza” and Sassari University both by mechanical alloying [6] and chemical precipitation from aqueous solutions [19]. The electrodes were prepared by dispersing in NMP the active material (AM), carbon black and PVDF in the wt.% ratios 82:10:8 and the slurry was cast on a copper substrate by doctor blade technique. These electrodes, tested with deep lithiation/delithiation galvanostatic cycles in EC:propylene carbonate (PC)-1 M LiClO_4 , displayed enhanced electrochemical performance reaching at the first few cycles a specific capacity value of 800 mAh g^{-1} UM, near to the nominal value. The cycling stability, however, is not yet satisfactory probably due to a not yet optimized electrode structure. Fig. 2 shows the cycling data related to a lithiated SnSb intermetallic alloy, $\text{Li}_4\text{Sn}_{0.72}\text{Sb}_{0.28}$, prepared by mechanical alloying at Sassari University from a mixture of Sn, Sb and Li under hexane with a shaker mill for 30 h. The electrodes were prepared from active material, carbon black Super P and PVDF in the wt.% ratio 82:10:8 and on a surface-roughened copper foil in argon atmosphere and tested in EC:PC-1 M LiClO_4 . The basic idea for choosing this lithiated material was to start

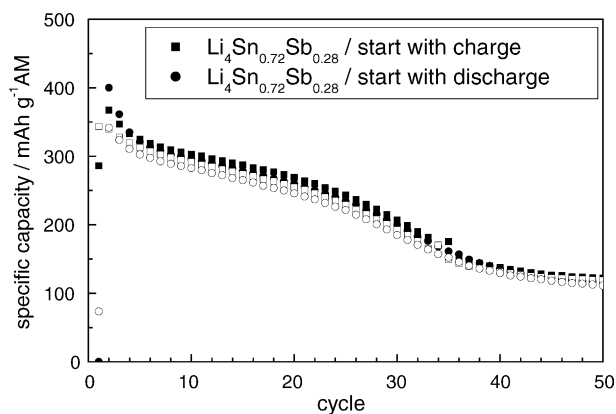


Fig. 2. Galvanostatic cycling tests at 120 mA g^{-1} of $\text{Li}_4\text{Sn}_{0.72}\text{Sb}_{0.28}$ electrodes (solid symbols, charge; open symbols, discharge) in the voltage range 0.02 and 1.50 V vs. Li (by permission of Trans Tech Publication [6]).

with an already charged and expanded host material, but the experimental data over 50 cycles demonstrated that, at least in this case, this strategy is not so beneficial as expected [6]. In Fig. 2 and in all the paper we call “charge” the lithiation process as if the electrode under study was working in a lithium-ion battery during the charge process.

The study on Cu_6Sn_5 , carried out at Bologna University, has been focused on the use of a new substrates to be used as current collector instead of conventional copper foil [8]. The substrate we examined was carbon paper (CP) which, with its three-dimensional interconnected carbon fibers, is able to host micrometric and submicrometric aggregates of mechanochemical and electrochemical Cu_6Sn_5 . The idea was that CP could be more pliant than copper to prevent the loss of electric contact during repeated lithiation–delithiation cycles. From Rietveld analysis of XRD patterns, the crystallite size of mechanochemical powder Sn:Cu 45.5:54.5 atomic ratio prepared at Sassari University by 25 h ball milling of Sn and Cu is 20 nm. The electrodes were prepared by permeating throughout CP a suspension of mechanochemical Cu_6Sn_5 in acetone, without addition of carbon additive and with only 4 wt.% PVDF binder, and by electrochemical deposition on CP and on Cu foil of Cu_6Sn_5 from aqueous solution [8]. The SEM images of the electrodes on CP in Fig. 3 show that the mechanochemical alloy is localized where the carbon fiber criss-cross, and that the electrodeposited Cu_6Sn_5 homogeneously covers the CP fibers. Despite the different distribution of the coverage, electrodes made with mechanochemical and electrochemical Cu_6Sn_5 , which both exhibit particle $<1 \mu\text{m}$, do not evidence differences in the electrochemical behaviour. Fig. 4a compares the cycling performance of two electrodeposited Cu_6Sn_5 electrodes, one on conventional copper foil and the others on CP having electrode mass loading quite similar, and of two mechanochemical electrodes of lower and higher mass loading on CP so as to enhance specific capacity and capacity per area unit, respectively. The reported data over cycling are the discharge specific capacity values of galvanostatic cycles at 0.74 mA cm^{-2} with time-limited charge for lithium insertion up to defined Li/Sn atomic ra-

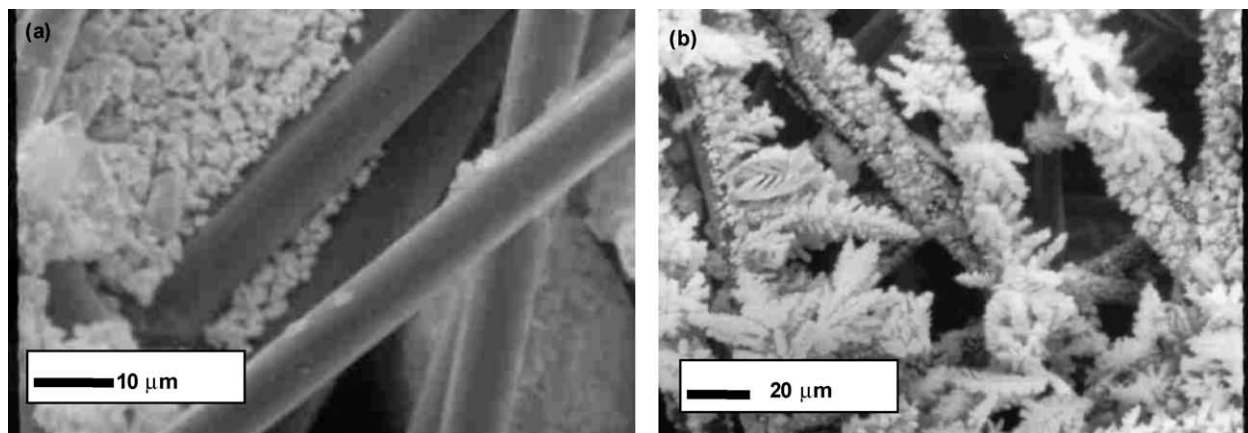


Fig. 3. SEM images of (a) mechanochemical and (b) electrochemical Cu_6Sn_5 on Spectracorp 2050 carbon paper.

tio (see Fig. 4 caption) and with cut-off voltages of 0.005 and 2.000 V versus Li. Whereas the capacity drastically decreases when copper substrate is used, so that the value of Li/Sn ratio of 1.88 is attained only for the first cycle, with CP the delivered capacity is constant over 250 tested cycles; to our knowledge these are the best cycling stability values for Cu_6Sn_5 . Fig. 4b shows the voltage profile of the 120th cycle of the $\text{Cu}_6\text{Sn}_5/\text{CP}$ electrode (E) of Fig. 4a with high mass loading and stable over 150 cycles (solid line) compared with the 120th of the bare carbon paper (dotted line), which being a carbonaceous material is able to insert lithium, but not at the same extent and with the same stability of $\text{Cu}_6\text{Sn}_5/\text{CP}$ electrode. The SEM images in Fig. 5 compare the Cu_6Sn_5 status of two electrodes, one with copper and the other with CP as current collector after cycling. These images evidence that copper foil, unlike the CP, is unable to support the mechanical stress of the Cu_6Sn_5 during lithiation–delithiation, which results in delamination of the alloy and loss of electric contact with cracks up to 20 μm wide.

Magnesium silicides have been prepared at Sassari University and electrochemically tested at Roma “La Sapienza” University [6]. Mg_2Si was prepared from Mg and Si both by mechanical alloying with an home-made mono-axial vibrating mill [20], and by SHS in Ar filled reaction camera [21]. Unlike the MA synthesis which yielded nanometric primary particles, the SHS method does not. Also lithiated magnesium silicide, $\text{Li}_4\text{Mg}_2\text{Si}$, was synthesized by MA of Li and Mg_2Si obtained by SHS. The electrochemical tests were performed on electrodes prepared from active material, carbon black Super P and PVDF in the wt.% ratio 82:10:8 on a surface-roughened copper foil in argon atmosphere and tested in EC:PC–1 M LiClO_4 . The charge/discharge galvanostatic cycles on Mg_2Si composites showed a specific capacity higher than 1000 mAh g^{-1} at the first cycle which, however, rapidly decreases. This behavior is typical of materials, which show mechanical disintegration and loss of electric contact. Hence, although the size of the primary particles of the material obtained by MA is in the nm-range, the overall material is

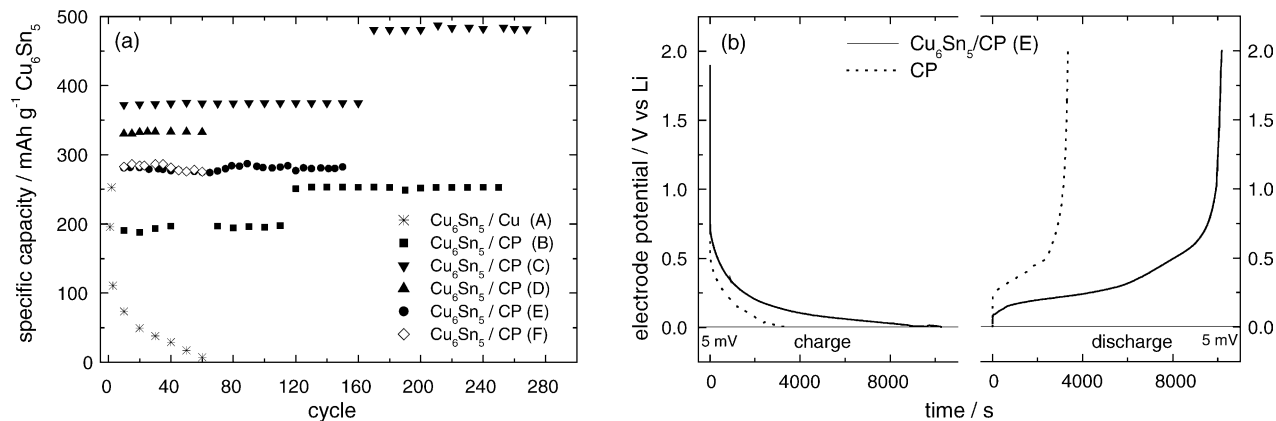


Fig. 4. (a) Discharge specific capacity from galvanostatic charge/discharge cycles at 0.74 mA cm^{-2} ($A = 0.68 \text{ cm}^2$) of electrochemical $\text{Cu}_6\text{Sn}_5/\text{Cu}$ (electrode A) and $\text{Cu}_6\text{Sn}_5/\text{CP}$ (electrode B), and of mechanochemical $\text{Cu}_6\text{Sn}_5/\text{CP}$ (electrodes from C to F) at different amounts of lithium inserted. The Li/Sn mol ratio, time of charge for $\text{Cu}_6\text{Sn}_5/\text{CP}$, and the mass of Cu_6Sn_5 are, respectively: (A) Li/Sn 1.88, 1 h 30 min, 4.3 mg cm^{-2} ; (B) Li/Sn 1.44 and 1.84, 1 h 30 min and 1 h 55 min, 5.6 mg cm^{-2} ; (C) Li/Sn 2.73 and 3.50, 1 h 30 min and 1 h 55 min, 3.0 mg cm^{-2} ; (D), Li/Sn 2.43, 3 h 00 min, 6.6 mg cm^{-2} ; (E) Li/Sn 2.02, 2 h 54 min, 7.5 mg cm^{-2} ; (F) Li/Sn 2.08, 3 h 54 min, 10.0 mg cm^{-2} . (b) Voltage profiles of the 120th galvanostatic charge/discharge cycles of mechanochemical $\text{Cu}_6\text{Sn}_5/\text{CP}$ electrode (E) and of bare CP.

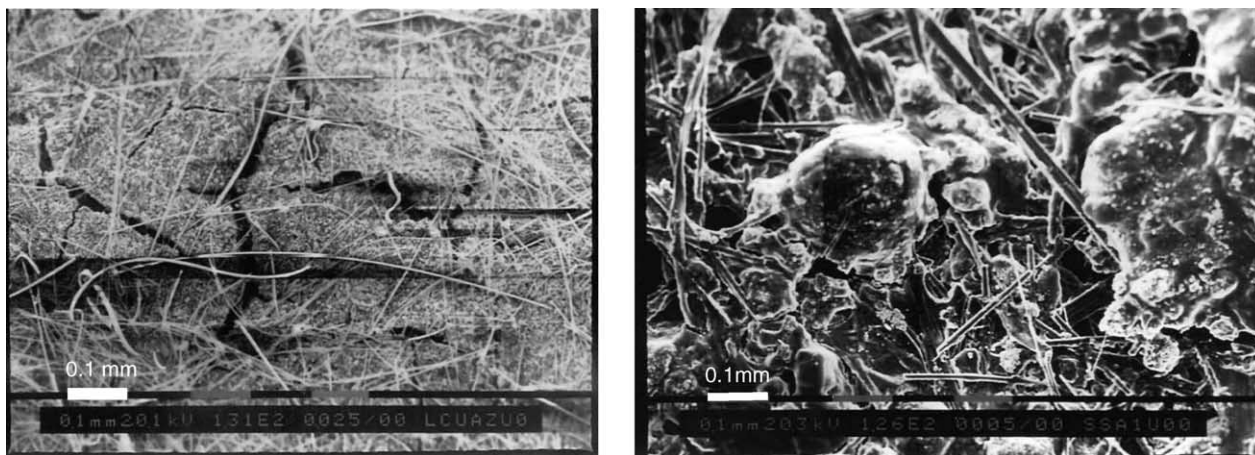


Fig. 5. SEM images of (a) electrochemical Cu_6Sn_5 on Cu current collector and of (b) mechanochemical Cu_6Sn_5 on CP current collector after cycling.

too dense to be stable over cycling. A different behavior was found for the related lithiated material, $\text{Li}_4\text{Mg}_2\text{Si}$. The idea to start with an already lithiated and expanded host to avoid the volume increase during the first cycle, in this case, had a beneficial impact on the cycling stability, as shows Fig. 6 which reports the cycling stability of electrodes of Mg_2Si and $\text{Li}_4\text{Mg}_2\text{Si}$, even if the capacity of the pre-lithiated material is lower than that of the unlithiated one.

Transition metal phosphides are an emerging class of anode materials and the group of Camerino University prepared, characterized and electrochemically tested the new NiP_2 [13]. Two synthesis routes were pursued to obtain NiP_2 , the tin-flux technique [22] and the mechanical milling of Ni and red P under Ar [13]. The NiP_2 obtained by MM displayed aggregates of 0.5–10 μm , smaller than those of NiP_2 from tin-flux technique. The cycling galvanostatic tests of NiP_2 composite (65 wt.% active material, 20 wt.% acetylene black and 15 wt.% PVDF) on Ni foil were performed in EC:DMC–1 M LiPF_6 . The first charge process, in which there is the formation of Li_3P with Ni segregation, is characterized by the uptake of six lithium corresponding to a nominal capacity of

1330 mAh g^{-1} ; on discharge four lithium are extracted, yielding LiP and leading to a cyclable capacity of 885 mAh g^{-1} , according to the following equations:

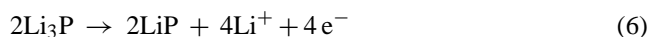
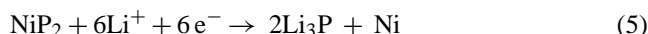


Fig. 7, however, evidences that after 10 cycles the discharge capacity is 460 mAh g^{-1} and seems to stabilize at 290 mAh g^{-1} after 20 cycles. In order to further investigate the system, LiP was prepared by high-energy mechanical milling of Li and red P under argon. The SEM image LiP displays aggregates of 1–2 μm , as Fig. 8 shows. A LiP composite electrode was prepared in dry box by mixing LiP :nanosize Ni powder in 2:1 mol ratio and adding 20 wt.% carbon black and 20 wt.% PVDF. This composite shows a better reversible capacity than NiP_2 , as shown in Fig. 7, but also a higher reactivity on air that makes it less easy to handle. The reaction of NiP_2 with lithium is comparable to that reported for CoP_3 .

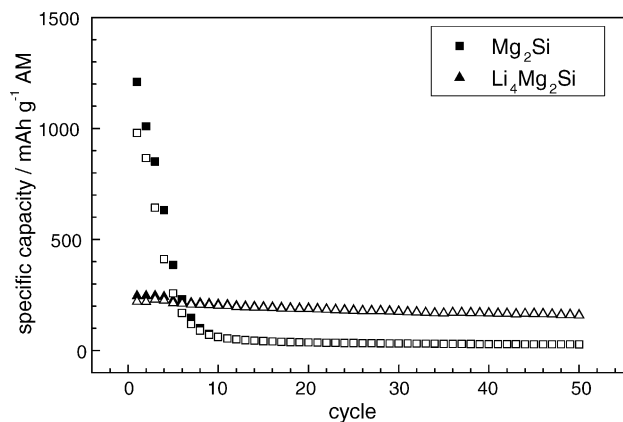


Fig. 6. Galvanostatic cycling tests at 120 mA g^{-1} of Mg_2Si and of $\text{Li}_4\text{Mg}_2\text{Si}$ electrodes (solid symbols, charge; open symbols, discharge) in the voltage range 0.02 and 1.00 V vs. Li [6].

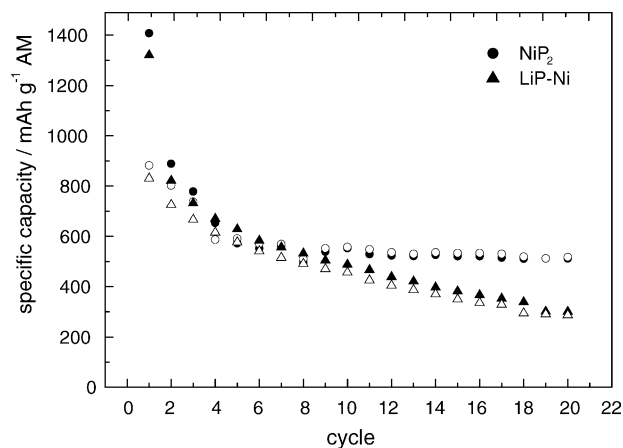


Fig. 7. Galvanostatic cycling tests at C/10 rate of NiP_2 composite electrode in the voltage range 0.05 and 1.70 V vs. Li and of LiP-Ni composite electrode in the voltage range 0.01 and 2.00 V vs. Li (solid symbols, charge; open symbols, discharge) (courtesy of Professor Roberto Marassi, Camerino University).

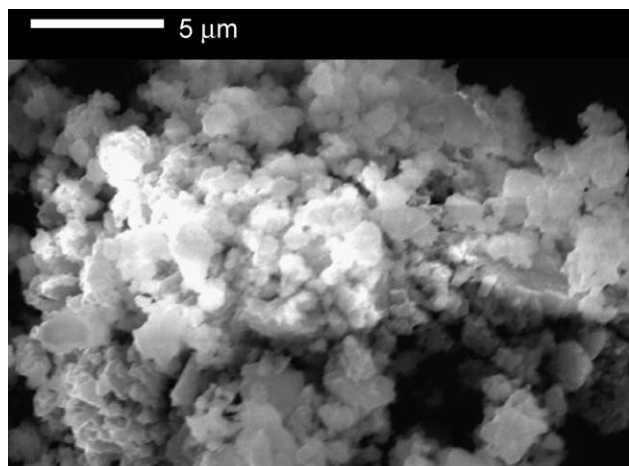


Fig. 8. SEM of LiP synthesized by mechanical milling method (courtesy of Professor Roberto Marassi, Camerino University).

As cathode materials are concerned, iron phosphate and lithium iron phosphate have been investigated by Rome “La Sapienza” and Chieti Universities. $\text{RuO}_2\text{-FePO}_4$ composites and carbon covered LiFePO_4 have been prepared via new sol–gel routes, starting from cheap Fe(III) salts at Chieti University. The synthesis of RuO_2 added– FePO_4 composites involved a dispersion of low particle size RuO_2 in the synthesis solution, yielding a composite materials with RuO_2 uniformly distributed throughout the α -quartz FePO_4 mass. The RuO_2 effect is beneficial in enhancing electronic conductivity, thus improving the kinetics of the electrochemical processes of this material and, consequently, the cyclability [14].

A new sol–gel route in Ar/H_2 atmosphere for the synthesis of an improved LiFePO_4 covered by carbon was successfully pursued at Chieti University, starting from Fe(III) salt:ascorbic acid:lactose (as carbon precursor) in the mol ratios 1:0.3:0.3. Fig. 9 shows the electrochemical performance in EC:diethylcarbonate (DEC)–1 M LiClO_4 of a LiFePO_4/C

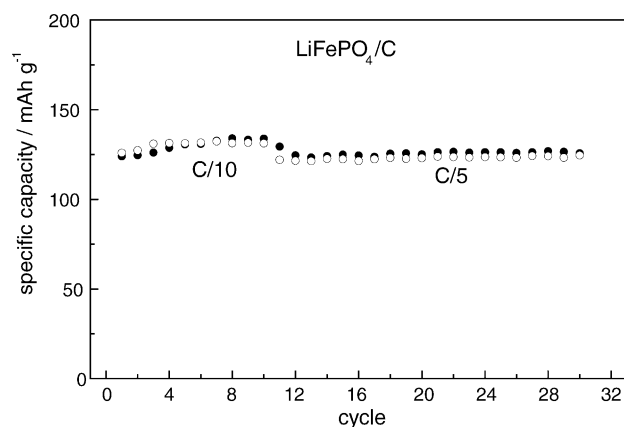


Fig. 9. Galvanostatic cycling tests at C/10 and C/5 rates LiFePO_4/C composite electrode thermally treated at 730° for 12 h in Ar/H_2 flux (solid symbols, charge; open symbols, discharge) (courtesy of Professor Fausto Croce, Chieti University).

electrode having 70 wt.% of nanometric LiFePO_4/C composite (thermally treated at 730° for 12 h in Ar/H_2 flux), 20 wt.% Super P carbon and 10 wt.% PVDF; this electrode displays a high specific capacitance, constant over 30 cycles, also at C/5 rate. This successful result indicates that LiFePO_4/C can match the goal of cathode material of low cost and environmental compatibility [15].

As the electrolytes are concerned, Chieti and Rome “La Sapienza” Universities are pursuing the strategy of solvent-free polymer electrolytes, i.e. blends of PEO-lithium salts with dispersed ceramic powders of nanometric size which improve significantly the ionic conductivity. Nanocomposite electrolyte formed by dispersing zirconia powder in $(\text{PEO})_{20}\text{LiCF}_3\text{SO}_3$ matrix exhibits ionic conductivity higher than in plain polymer [17]. PEO-LiX membranes with lithium salts having large plasticizing anions, such as lithium bisoxalateborate (LiBOB) have also been studied, and has been evidenced the plasticizing role of the large lithium salt anion. Work is in progress to further enhance the conductivity of this new polymer electrolyte by dispersing in its bulk selected nanometric ceramic powders [18].

At this stage of the Project some remarks can be done. By selecting appropriate synthesis routes, all the envisaged electrode materials have been prepared with primary particles at nanometric or submicrometric level.

As anode materials are concerned, graphite-nanosize Cu composite retains 40% of its capacity at -30°C , a relevant result for lithium-ion batteries operating at low temperature. Nanostructured intermetallic alloy like SnSb still displays high capacity loss over cycling even when lithiated intermetallic alloys are used as electrode materials; a reduction of the lithiation level could be beneficial for cycling stability. Intermetallic Cu_6Sn_5 hosted in a such three-dimensional conductive matrix as carbon paper, with its micrometric interconnected fibres, displays cycling stability over more than 100 cycles, demonstrating the key-role of the current collector-substrate morphology. Mg_2Si , even at nanometric level, does not display good cycling stability; improved cyclability has been obtained for lithiated magnesium silicides. LiP with nanosize Ni powder displays a better reversible specific capacity and cycling stability than NiP_2 , but also a higher reactivity in air.

On the line of cathode materials, new synthesis methods yielded nanometric LiFePO_4/C composites, very promising positive electrode materials for new generation lithium-ion batteries.

As it concerns the electrolytes, the performance of PEO-lithium salt-nanosize additive membranes confirms the beneficial effect on conductivity of nanosize-ceramic’s addition.

Acknowledgments

The authors acknowledge MIUR (Project COFIN2002 prot. 2002032512), the project partners Professors G. Cocco (University of Sassari), F. Croce (University of Chieti), R.

Marassi (University of Camerino), N. Penazzi (Politecnico di Torino) and B. Scrosati (University of Roma “La Sapienza”), who is also the Project Coordinator, and all the researchers still working on this Project.

References

- [1] M. Borghini, M. Mastragostino, A. Zanelli, G.B. Appetecchi, F. Croce, B. Scrosati, M. Conte, S. Passerini, P.P. Prosini, P.G. Bernini, S. Saguatti, *AEI* 85 (3) (1998) 62/222–64/224.
- [2] M. Mastragostino, F. Soavi, A. Zanelli, *J. Power Sources* 81/82 (1999) 729–733.
- [3] S.S. Zhang, K. Xu, T.R. Jow, *Electrochim. Acta* 48 (2003) 241–246.
- [4] R. Marassi, F. Nobili, T. Mecozzi, S. Doske, 205th Electrochemical Society Meeting, San Antonio (TX), 2004 (Abstract 94).
- [5] J. Yang, M. Winter, J.O. Besenhard, *Solid State Ionics* 90 (1996) 281–287.
- [6] M. Wachtler, L. Schiffini, I. Amadei, J. Serra Moreno, B. Scrosati, G. Cocco, *J. Metastable Nanocryst. Mater.* 20/21 (2004) 263–268.
- [7] K.D. Kepler, J.T. Vaughey, M.M. Thackeray, *Electrochem. Solid State Lett.* 2 (1999) 307–309.
- [8] C. Arbizzani, M. Lazzari, M. Mastragostino, *J. Electrochem. Soc.* 152 (2005) A289–A294.
- [9] D.C.S. Souza, V. Pralong, A.J. Jacobson, L.F. Nazar, *Science* 296 (2002) 2012–2015.
- [10] R. Alcántara, J.L. Tirado, J.C. Jumas, L. Monconduit, J.O. Fourcade, *J. Power Sources* 109 (2002) 308–312.
- [11] D.C.S. Souza, V. Pralong, G. Ouvrard, L.F. Nazar, 11th International Meeting on Lithium Batteries, Monterey, CA, 2002 (Abstract 60).
- [12] K. Wang, J. Yang, J. Xie, B. Wang, Z. Wen, *Electrochem. Commun.* 5 (2003) 480–483.
- [13] R. Marassi, in preparation.
- [14] F. Croce, A. D’Epifanio, P. Reale, L. Settini, B. Scrosati, *J. Electrochem. Soc.* 150 (2003) A576–A581.
- [15] F. Croce, L. Settini, B. Scrosati, in preparation.
- [16] F. Croce, C. Sides, B. Scrosati, C. Martin, *Electrochem. Solid State Lett.*, submitted for publication.
- [17] A. D’Epifanio, F. Serraino Fiory, E. Traversa, S. Licocchia, F. Croce, B. Scrosati, *J. Appl. Electrochem.* 34 (2004) 403–408.
- [18] D. Zane, G.B. Appetecchi, B. Scrosati, 12th International Meeting on Lithium Batteries, Nara (Japan), 2004 (Abstract 364).
- [19] H. Mukaibo, T. Osaka, P. Reale, S. Panero, B. Scrosati, M. Wachtler, *J. Power Sources* 132 (2004) 225–228.
- [20] F. Delogu, M. Monagheddu, G. Mulas, L. Schiffini, G. Cocco, *Int. J. Non-Equilib. Process* 11 (2000) 235.
- [21] M. Monagheddu, S. Doppiu, C. Deidda, G. Cocco, *J. Phys. D: Appl. Phys.* 36 (2003) 1.
- [22] D. Elwell, H.J. Scheel, *Crystal Growth from High Temperature Solutions*, Academic Press, London, 1975.