A novel synthetic procedure for the preparation of a SiO$_x$-based nanocomposite, involving gelification of resorcinol-formaldehyde and tetraethyl orthosilicate, is reported. The composite is characterized as an anode material in a lithium-ion battery. The micrometric, amorphous material has a characteristic nanostructured configuration and shows an electrochemical process involving both the alloying of Li–Si and the insertion of Li into the hard carbon matrix. The electrode reveals in a lithium half-cell a relatively low impedance and a reversible capacity ranging from 650 mAh g$^{-1}$ at the lower current, to 400 mAh g$^{-1}$ at high current regimes, with a cycle life extending to 200 cycles. The anode is combined with a high-voltage LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinel cathode in a 4.3 V lithium-ion battery delivering a capacity of about 115 mAh g$^{-1}$ and operating at the high rate of 5C. The suitable synthesis pathway, the low cost and the promising electrochemical behavior suggest the nanocomposite anode for application in high-performance lithium-ion battery.

1. Introduction

Rechargeable batteries with high energy and low cost are attracting large efforts due to the continuous and rapid development of the renewable energy and electric vehicles markets.[$^{[1]}$] Photovoltaic power plants require efficient and low cost energy storage systems, while EVs need satisfactory driving autonomy and safety levels, hence high energy and stable batteries.[$^{[2]}$] To meet these requirements a change of the electrode and the electrolyte components is necessary, i.e. moving from conventional graphite anode, LiCoO$_2$ cathode and carbonate based electrolytes to new-chemistry electrodes and electrolytes, characterized by high capacity, low costs and enhanced safety level.$^{[1,3]}$ Silicon is considered very promising anode since abundant, cheap and characterized by very high theoretical capacity in lithium cell, i.e. of about 4000 mAh g$^{-1}$, that is much greater than that ascribed to graphite anode (370 mAh g$^{-1}$).[$^{[4]}$] The large volume variation during the Li–Si alloying de-alloying process leading to rapid electrode disintegration has been recently addressed by incorporating silicon nanoparticles in carbon matrix of various natures, in analogy with the procedure adopted for producing tin-carbon nanocomposites.$^{[5–12]}$ Despite a lower electrochemical activity in respect to silicon, silicon oxide nanoparticles attracted great attention in the recent years in view of the excellent stability of the material in lithium cells, ascribed to the buffering action of the various silicate species formed by the first lithiation process.$^{[13]}$ High voltage lithium transition metal oxides, i.e. LiMO$_x$ with spinel structure triggered an increasing interest as cathodes due to their high power and energy density compared to standard lithium cobalt oxide electrode.$^{[14–16]}$ Among them, LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and Li[Ni$_{0.45}$Co$_{0.1}$Mn$_{1.45}$]O$_4$ demonstrated enhanced properties, such as relevant rate capability and good cycle life in lithium ion battery.$^{[17–21]}$ Indeed, the use of high voltage cathode materials characterized by good rate capability simultaneously allows high energy density and power, i.e., key requirements for application in electric vehicles. In this paper we studied a SiO$_x$-based composite anode prepared by a simple synthetic pathway involving the formation of a resorcinol-formaldehyde gel and its calcination under argon.$^{[22–24]}$ The material revealed an amorphous structure and a micrometric morphology in which the SiO$_x$ nanoparticles with dimension of about 15 nm are trapped in a carbon matrix. The composite has been successfully studied in lithium half-cell as well as in high-voltage lithium ion battery using a LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode. The half-cell delivered a high stable capacity, while the full lithium-ion battery demonstrated remarkable cycle life and rate capability, thus suggesting the SiO$_x$-based composite as a high-performance and low-cost anode material for application in advanced energy storage systems.

Experimental Section

Synthesis

SiO$_x$-based composite was synthesized by sol-gel method. 18 g of resorcinol and 58.5 g of formaldehyde were mixed at room temperature. After the complete dissolution of the resorcinol, 21 g of tetraethyl orthosilicate (TEOS) were added. The obtained solution was heated up at 70 °C and 2 ml of a 1 M HCl solution was added dropwise to catalyze the gelification reaction. A pink semitransparent homogeneous gel was obtained after 5 minute (Figure 1a). The obtained gel was aged for 24 hours at room T, until dark orange gel was obtained (Figure 1a). The gel was then cut into small pieces and washed with ethanol in order to remove HCl residual. Finally, the gel was annealed at 1000 °C for 10 h under Ar-H$_2$ 5% atmosphere. The particle size of the annealed compound was reduced by using a mortar and a sieving system with a mesh size of 45 μm. The final composition of the composite in terms of SiO$_x$-based products to carbon weight ratio was 25:75, as revealed by thermogravimetric analysis (TGA) reported in Figure S1a in the Supporting Information. The TGA was performed in the temperature range 25 °C–950 °C under air flux (60 ml min$^{-1}$) by heating at...
The material structure was characterized by using a Rigaku D-max Ultima + X-ray diffraction system with a Cu Kα radiation source, while its morphology was detected by scanning electron microscopy (SEM) using a Phenom-Fei scanning electron microscope and by transmission electron microscopy (TEM) using a Zeiss EM 910 microscope, equipped with a tungsten thermos-ionic electron gun operating at 100 kV.

The negative and the positive electrodes were prepared as thin film by doctor-blade deposition of a slurry composed of 80 % active material, 10 % PVDf 6020 (Solef Solvay) as binder and 10 % SP–C65 (Imerys) as electron conductor. Copper and aluminum substrate were used for the anode and the cathode electrode, respectively. The active material loading was of 2.5 mg/cm² and of 4.8 mg/cm² for the anode and the cathode, respectively.

The electrochemical process of the SiO₂-based material was studied by Potentiodynamic Cycling with Galvanostatic Acceleration (PCGA). The test was carried out in 3-electrode configuration T-cell by Potentiodynamic Cycling with Galvanostatic Acceleration (PCGA). The test was performed using a Maccor Series 4000 Battery Test System at room temperature (25 °C). Electrochemical impedance spectroscopy (EIS) of the anode material was performed in lithium ion-cell cycled at a current of 50 mA g⁻¹, in the 0.01–2 V voltage range. The test was performed using a 3-electrode T-cell equipped with lithium probe as the reference electrode. The impedance spectra were acquired at the OCV and at end of the charge process in the frequency range of 1 MHz-10 mHz using 10 mV signal amplitude with VSP Biologic Science Instrument.

2. Results and Discussion

Figure 1 summarizes the synthesis procedure of the SiO₂-based anode (Figure 1a), and shows its characteristics in terms of morphology (SEM, Figure 1b), particles size (TEM, Figure 1c) and structure (XRD, Figure 1d). The synthesis involves acid gelification of resorcinol, formaldehyde (precursors of the carbon), and TEOS (precursor of the SiO₂). The homogenous viscous solution changes color from light pink to dark orange by aging, and completely vitrifies due to time promoted cross linking of the gel (Figure 1a). The final thermal treatment (calcination) under Ar–H₂ of the glassy gel leads to the formation of a SiO₂-based composite, represented by a sketch in Figure 1a which shows the expected morphology of the compound: the white sphere indicates the silicon-based nanoparticle entrapped within the carbon matrix, i.e., the black part in the sketch. Figure 1b reveals the morphology of the SiO₂-C composite, which is formed by large carbon domains with a size of the order of 40–50 μm, and smaller particle at the surface. These carbon domains entrap the silicon or silicon oxide nanoparticles which are revealed by the inside view of the carbon domain in the TEM image of Figure 1c. The dark particles in the TEM image characterized by an average dimension of 15 nm represent the silicon, which has the higher atomic number, while the light surrounding matrix represents the carbon.

The amorphous nature of the synthesized material is evidenced by Figure 1d reporting the diffraction pattern of the composite. The figure reveals the absence of crystalline reflections ascribed to SiO₂ compounds, while the broad diffraction signals around 22°, 44° and 80° of 20 can be ascribed to the reflection of (002), (100) and (110) graphite plans of the amorphous carbon. These characteristic structure and morphology are expected to reflect electrochemical stability, high tape-density and simultaneously low surface

10 °C min⁻¹. The LiNi₀.₅Mn₁.₅O₄ cathode material was synthesized as reported in previous paper.⁵

Characterization

The material structure was characterized by using a Rigaku D-max Ultima + X-ray diffraction system with a Cu Kα radiation source, while its morphology was detected by scanning electron microscopy (SEM) using a Phenom-Fei scanning electron microscope and by transmission electron microscopy (TEM) using a Zeiss EM 910 microscope, equipped with a tungsten thermos-ionic electron gun operating at 100 kV.

The negative and the positive electrodes were prepared as thin film by doctor-blade deposition of a slurry composed of 80 % active material, 10 % PVDf 6020 (Solef Solvay) as binder and 10 % SP–C65 (Imerys) as electron conductor. Copper and aluminum substrate were used for the anode and the cathode electrode, respectively. The active material loading was of 2.5 mg/cm² and of 4.8 mg/cm² for the anode and the cathode, respectively.

The electrochemical process of the SiO₂-based material was studied by Potentiodynamic Cycling with Galvanostatic Acceleration (PCGA). The test was carried out in 3-electrode configuration T-cell by setting stepwise potential scans of 5 mV with a minimum current limit of 25 μA (corresponding to ca. 1/100 C), within a 0.01–2 V voltage range, using a Bistat Biologic-Science Instruments.

The SiO₂-based material was characterized by galvanostatic cycling in 2-electrode configuration T-type lithium half-cells. The active material was used as the working electrode, a 1 M solution of LiPF₆ in ethylene carbonate-dimethyl carbonate (EC:DMC, 1:1 w:w, Merck Battery Grade) soaked into a Whatman/C24 separator as the electrolyte, and a lithium metal foil as counter/reference electrode. The galvanostatic cycles have been performed by a current ranging from 50 mA g⁻¹ to 400 mA g⁻¹ within 0.01–2 V voltage limits. The
reactivity as indeed observed for similar materials based on lithium alloying reaction. However, the absence of relevant crystallinity and the very small size of the inside particles avoid the determination of the oxidation state of the silicon, which is therefore indicated by SiOx. This aspect needs certainly further investigation which is indeed in progress in our laboratory. The presence of the silicon and its amount with respect to the carbon have been evaluated by coupling TGA and XRD measurement, as well as by EDX mapping as reported in Figure S1 in the Supporting Information. The TGA under air of the composite (Figure S1a) reveals a residual of 25% in weight after carbon removal by oxidation with formation of CO2, which is mainly composed of SiO2 according to the diffraction pattern of Figure S1b. Furthermore, EDX mapping of the composite (Figure S1c) shows the dispersion of the silicon within the composite, while the elemental analysis confirms the silicon to carbon ratio already revealed by TGA.

The composite anode has been investigated by the Potentiodynamic Cycling with Galvanostatic Acceleration (PCGA). This quasi-equilibrium technique allows the detailed characterization of the electrochemical process. The differential capacity versus potential profile of the PCGA reported in Figure 2a shows during the initial discharge process (lithiation) various peaks. A first irreversible peak at about 0.8 V vs. Li (marked by 1 in Figure 2a) is associated with the reduction of the electrolyte with formation of a solid electrolyte interface (SEI) film. A second irreversible peak at about 0.3 V vs. Li (peak 2 in Figure 2a) is associated with the reduction of SiOx compounds, with predominant formation of silicon and Li2O. However, literature works suggested possible formation of side products composed of silicates, such as Li2SiO4 or Li2Si2O5, during this irreversible stage which may buffer the mechanical stress associated to the alloying of lithium with silicon.

The two reversible peaks at about 0.1 V vs. Li (peaks 3 in Figure 2a) can be associated to the insertion of the lithium in the amorphous carbon matrix, while the alloying process of the lithium with the silicon formed during the first reduction may be observed at about 0.3–0.4 V vs. Li (peaks 4 in Figure 2a). The SiOx-based anode is following characterized in lithium half-cell in order to determine its suitability for lithium–ion battery. Figure 2b shows the voltage signature of the cycling test performed at various currents (i.e., the 10th, 30th, 50th and 70th cycles performed at current density of 50, 150, 250, 350 mA g−1, respectively). The material can deliver a capacity of about 700 mAh g−1 at the lower current (50 mA g−1) and a capacity higher than 400 mAh g−1 at the higher current (350 mA g−1), with an average working voltage of about 0.4 V. The cycling trend of the multi-rate galvanostatic test above mentioned is reported in Figure 3c. The figure evidences the relevant response the electrode at the various currents, with capacity gradually changing and efficiency of about 99%. Figure 2 in Supporting information reports the long terms cycling performance of the electrode at a selected current (400 mA g−1) which is considered a practical value for cell application, e.g., higher than the 1C current of the conventional graphite (370 mA g−1). The figure shows a capacity of about 700 mAh g−1 during the first discharge and a very stable reversible capacity of about 400 mAh g−1 during the following 200 cycles. However, the SiOx based electrode shows low efficiency during the first cycle (43%, see Figure S2 in Supporting Information) which is associated in part with the decomposition of the electrolyte during the initial reduction process with solid electrolyte interphase (SEI) film formation at the electrode surface and in part with the reduction of
and the LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} spinel cathode at 1C current.

d) Rate capability test of the lithium-ion cell at a current of C/5, C/3, C/2, 1C, 2C and 5C cycling tests of lithium-ion cells employing the SiO\textsubscript{x} compounds to silicon, lithium oxide and side products\textsuperscript{[13, 33]} already observed during PCGA test of Figure 2a.

Figure 3. a) Voltage profile, and b) cycling response of the galvanostatic cycling tests of lithium-ion cells employing the SiO\textsubscript{x}-based composite anode and the LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} spinel cathode at 1C current. d) Rate capability test of the lithium-ion cell at a current of C/5, C/3, C/2, 1C, 2C and 5C (1C = 148 mA g\textsuperscript{-1}). Electrolyte EC:DMC (1:1), 1 M LiPF\textsubscript{6}. Voltage limits 4.9–2.6 V. Room temperature (25 °C).

The SiO\textsubscript{x}-based anode is herein coupled with a LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} high voltage spinel\textsuperscript{[18, 25]} to form a high voltage lithium-ion battery. Figure 3a-b reports the voltage signature and cycling performances of the full cell galvanostatically cycled at a 1C rate (148 mA g\textsuperscript{-1}). Figure S4a shows a first conditioning cycle in which both the anode and the cathode reach the steady state conditions\textsuperscript{[25]} and reproducible subsequent cycles characterized by an average working voltage of about 4.3 V, reflecting the combination of anode and cathode profiles, and a reversible capacity of 110 mAh g\textsuperscript{-1}, i.e., 75% of the theoretical value of LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4}\textsuperscript{[18, 25]} The cyclic response of Figure S4b reveals a remarkable efficiency and cycling stability, extended up to 200 charge-discharge cycles with a coulombic efficiency higher than the 99% upon stabilization. This excellent behavior suggests optimized cell configuration both in terms of electrodes-electrolyte compatibility, cell balance and electrodes stability. Figure 3c shows the cycling trend of the full cell at increasing current rates, i.e. C/5, C/3, C/2, 1C, 2C and 5C (1C = 148 mA g\textsuperscript{-1}), while Figure S4a in Supporting Information reports the corresponding voltage profiles. The figures evidence remarkable rate capability, with capacity ranging from 120 mAh g\textsuperscript{-1} at C/5 (80% of the theoretical value) to the still acceptable value of 75 mAh g\textsuperscript{-1} (50% of the theoretical value) at a current rate as high as 5C, corresponding to a complete charge/discharge by only 12 minutes. The theoretical specific energy and the power activation cycles both in Figure 2c (multi-rate test) and in Figure S2b (single rate test in Supporting Information). It is noteworthy that the electrodes collected from cell after cycling do not show relevant signs of deterioration, as indeed expected by the excellent electrochemical performances observed in Figure 2 and Figure S2, thus likely excluding a significant delamination by volume variation of the material upon operation, however minor electrode deterioration may be not completely excluded. The stability of the cell during cycling is further confirmed by the evaluation of the interphase resistance reported in Figure S3 in Supporting Information. The figure shows the electrochemical impedance spectra of the anode material in lithium cell at the pristine state, after the first, the fifth and the tenth cycle performed at a current of 50 mA g\textsuperscript{-1}. The electrode shows an initial reduction of the interphase resistance from the 200 Ω at the pristine state to 70 Ω upon the first cycle which as can be likely ascribed to the full wetting of the electrode as well as to possible structural reorganization of the material due to reduction of the silicon oxides to Si\textsuperscript{[13, 33]} During subsequent cycles Figure S3 shows a very stable interphase resistance of about 70 Ω.

Table S1 in the Supporting Information reports a comparison of the cycling response of the anode herein studied with respect to similar materials reported in literature. The table reveals a performance which is in line with anode materials based on silicon oxide precursors. Furthermore, the table shows a lower capacity of the SiO\textsubscript{x}-based materials with respect to those employing crystalline silicon, due to a higher theoretical capacity of the latter. On the other hand, the main advantages of our approach is the very simple and cheap synthetic pathway, and the relevant suitability for application in full lithium ion cell (see following discussion).

The silicon oxide compounds to silicon, lithium oxide and side products\textsuperscript{[13, 33]} already observed during PCGA test of Figure 2a. This initial inefficiency, which may actually affect the application of the anode material in full cell, is herein removed by pre-cycling the electrode in half lithium cell before use in lithium-ion battery (see the Experimental Section).

The steady state reversibility of the electrochemical process during cycling is well evidenced by the very good Coulombic efficiency which becomes higher than 99% after the initial
density of the system have been calculated by considering the cathode mass and reported in Figure S5b in Supporting Information. The figure reveals very promising characteristics of the battery such as a specific energy of about 500 Whkg⁻¹ at the lower current, 300 Whkg⁻¹ at the higher one and a maximum power density as high as 3000 Wkg⁻¹.

3. Conclusion

A high performance SiO₂-based anode for application in lithium-ion battery has been herein obtained by simple synthetic pathway. TG analysis, XRD SEM and TEM images suggested an amorphous material consisting of a carbon matrix including SiO₂ nanoparticles. However, the full identification of the electrode nature requires further analysis. The composite material revealed remarkable electrochemical characteristics in a half cell, such as a capacity ranging from 400 to 700 mAhg⁻¹ and stability extended over 200 cycles. The electrode has been employed as the anode in a lithium-ion battery using high-voltage LiNi₀.₅Mn₁.₅O₄ spinel cathode. The full cell evidenced very stable trend, high voltage and rate capability as well as energy and power values exceeding those ascribed to the common lithium-ion battery. These enhanced performances suggest the anode and the lithium-ion cell as suitable candidates for application in emerging fields such as the electric vehicles.[2,43]

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Conflict of Interest

The authors declare no conflict of interest.

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