Doped-Si–Ag composite electrodes for Li-ion batteries

Girikrishna Talla [a], Ramesh K. Guduru [b,c], Ben Q. Li [b,*], Pravansu S. Mohanty [b]

[a] Department of Electrical Engineering, University of Michigan, Dearborn, MI 48128, USA
[b] Department of Mechanical Engineering, University of Michigan, Dearborn, MI 48128, USA
[c] Presently at Department of Mechanical Engineering, Lamar University, Beaumont, TX - 77710, USA

ABSTRACT

An experimental study is carried out of the electrochemical characteristics of electrodes made from pure silicon (Si), doped-silicon (doped-Si) particles and doped-silicon–silver (doped-Si–Ag) composite particles. Doped-Si particles of 10–20 μm are obtained by mechanically crushing the silicon wafers, followed by sieving, and the doped-Si–Ag composite particles was prepared by self-selective electroless deposition. The Ag coating on doped-Si provides improved overall electrical conductivity that enables a better charge transfer. Measurements show that the doped-Si–Ag composite anode give the best electrochemical performance, with the lowest impedance and improved cyclability, and this is followed by the electrodes of doped-Si and pure Si. Moreover, the composite electrode has a stable discharge capacity of 1300 mAhrg^{-1} for more than 100 cycles, which is attributed to a good electrical integrity, while the pure and doped-Si electrodes degraded in less than 40 cycles.

© 2014 Published by Elsevier B.V.

1. Introduction

In recent years, there has been an increased demand for high energy density batteries to power the devices from portable electronics to automotive vehicles, which requires anode electrodes with a high specific energy capacity. Carbon based anodes have been in use in the industry for the past two decades, because of long cycle life, low cost, low toxicity, ease of production and small volume changes upon lithiation. However, their intrinsic energy capacity (~372 mAhrg^{-1}) [1–3] has now limited their applications, which has driven the researchers to explore for higher capacity anode materials, such as silicon (Si) and tin (Sn) etc. [4–6]. Similar to carbon, Si also lithitates at a low potential (~0.25 V) with respect to Li electrode, while exhibiting a specific capacity around ~4000 mAhrg^{-1}. This ability of a tenfold increase in energy storage capacity has generated considerable efforts to make a viable Si-based anode in the practical applications [7–14]. Although Si is a low cost and low toxic material with a high specific capacity, its large volume expansion (>300%) during lithiation usually results in particle breakage with a loss of structural integrity and electrical contact. This in turn causes poor cyclability, which has limited its commercialization [15–18]. Researchers have attempted to address these problems by employing nanoparticulate or thin film or nanotube/nanowire electrodes of Si. In thin film electrodes [19,20], the effect of volume expansion was showed to be mitigated by depositing a small amount of silicon on the electrodes. However, in the form of thin film electrodes, the overall capacity per unit volume is significantly limited. On the other hand, nanowire [21] and nanotube [22] electrodes showed a very good capacity retention for a large number of cycles, but their preparation requires expensive and time consuming fabrication techniques.

Pure silicon (Si) electrodes [11,12] with a particle size <20 μm were reported to show high initial capacity with a rapid decay within the first five cycles. However, by reducing their size to nanometer range [10] cyclability was extended up to 20 cycles. Tao Zhang et al. [13] demonstrated an improvement in the electrochemical characteristics of pure Si by coating with silver, and obtained a good initial capacity up to 1137 mAhrg^{-1}, which decreased gradually to less than 534 mAhrg^{-1} after 20 cycles.

In this study, we investigate the electrochemical performance of pure and n-type doped-silicon (doped-Si) electrodes (single crystal particles), and conductive silver coated doped-Si electrodes. To the best of our knowledge, this is perhaps the first attempt to use single crystalline <100> doped-Si particles obtained from a wafer as an anode material in lithium ion batteries. The electrodes of doped-Si have a lower impedance and higher cyclability compared with those of pure Si, and the anodes of silver covered doped-Si perform the best due to the enhanced electrical conductivity and electrode integrity.

2. Experimental procedure

2.1. Material selection

Pure Si with a particle size in the range of 1–20 μm (99.9985% metal basis, Alfa Aesar, USA) was sieved to select the particles in the range of

10–20 μm for electrode preparation. Doped-Si wafers (n-type, resistivity 2 Ω, Virginia Semiconductor Inc., USA) were mechanically crushed to obtain powders, and then sieved to obtain the particles in the range of 10–20 μm.

2.2. Synthesis of Si–Ag composite particles

Half a gram of doped-Si particles were added to a 20 ml of ultra-pure water (HPLC grade, Alfa Aesar, USA) and continuously stirred with a magnetic stirrer to avoid settling of the particles. Then two milliliters of a 1 M silver nitrate (AgNO3, purity >99.9%, Alfa Aesar, USA) was added dropwise while stirring with a constant speed. However, after adding 1 ml of $AgNO_3$, 200 μl of HF was added, and then the rest of the $AgNO_3$ was added. The $Ag+$ ions in the solution were reduced to form a silver coating on the silicon particles by self-selective electroless deposition. Then the doped-silicon–silver (doped-Si–Ag) particles collected after centrifuging the above solution were washed with ultra-pure water to remove traces of all the chemicals used. Finally, these powders were dried in a vacuum oven at 120 °C for 24 hours.

2.3. Electrode preparation

All the electrodes for electrochemical characterization were prepared by coating copper current collectors with a thin layer of carbon followed by silicon active material that was bladed on top of the carbon layer [23]. Carbon layer between copper foil and the active Si material was expected to provide a cushion effect to accommodate the volumetric strains during the charge–discharge process. Carbon slurry was prepared by mixing carbon and polyvinylidene fluoride (PVDF) binder in equal ratios by weight following the addition of N-methyl-2-pyrrolidone (NMP) solvent and ultra-sonication for 15 minutes. This mixture was then uniformly spread out on the copper foil (current collector) and vacuum dried at 90 °C for 4 hours. For the electrode material, a mixture containing silicon, PVDF and carbon black in the weight ratio of 70:20:10, respectively, was prepared, and then mixed with NMP solvent to form slurry. Thus the obtained slurry was bladed on top of the previously coated carbon layer, and vacuum dried at 120 °C for 12 hours. These electrodes were used in a coin cell assembly.

2.4. Cell assembly

Silicon electrode half-cells were constructed inside an argon filled glove box using 20 mm diameter coin cells (CR2032) with Celgard 2500™ separator, Li (reference electrode) and electrolyte (1 M LiPF$_6$ dissolved in ethylene carbonate (EC):dimethyl carbonate (DMC) − 1:2 solution). The crimped coin cells were placed in a stainless steel cell (MTI Corporation) for electrochemical characterization.

2.5. Electrochemical testing

Electrochemical characterization was carried out using BioLogic VMP3 multichannel analyzer. Galvanostatic charge–discharge of all the electrodes was done following a constant charge capacity (CCC) method by limiting the capacity up to 1300 mAhrg^{-1} as described in the references [9,24] with a controlled amount of Li-ion intercalation into Si anode while fixing the time period either for charging or discharging in order to improve the cycling stability. Capacity of the electrodes was calculated based on the silicon active material weight. The cyclic voltammetry analysis (CV) was performed between 0.05 and 2 V at a rate of 10 mV min^{-1}. Electrochemical impedance spectroscopy (EIS) tests were performed in a frequency range from 0.1 Hz to 10 kHz with an amplitude of 10 mV.

2.6. Microstructural characterization

Microstructural characterization of doped-Si–Ag composite particles was done using scanning electron microscopy (SEM) (Hitachi S-2600N) technique, and composition analysis was performed with energy dispersive x-ray (EDX) analysis technique on the SEM.

3. Results and discussion

3.1. Pure Si and doped-Si electrodes

EIS results of pure Si and doped-Si before and after cycling are shown in Figs. 1 and 2 respectively. In Fig. 1(a), the intercept on X-axis in the high frequency region indicates an internal resistance of the cell, and the diameter of the semicircle represents the effect caused by charge transfer and electrochemical double layer. The straight line at a 45° angle after the semicircle represents the resistance in the bulk electrode [25]. From the data shown in Figs. 1(a) and 2(a), it is evident that the impedance of doped-Si electrode is lower than the pure Si electrode.

Figs. 1(b) and 2(b) are the equivalent circuit models representing the impedance of the electrodes before and after cycling, respectively, R_s stands for the internal resistance of the cell, C_{dl} is the capacitance due to the electrode and the electrolyte interface, R_{ct} is the charge transfer resistance of the electrode interface, R_f and C_f are the film resistance and capacitance formed at the electrode and electrolyte interface after cycling, respectively, and Z_w denotes Warburg impedance representing the diffusion resistance for Li-ions in the bulk electrode. The values for all the elements shown in the equivalent circuits are given in Tables 1 and 2. Although R_s of both pure Si and doped-Si is in the same order, the R_{ct} and Z_w values are lower for doped-Si electrodes than for the pure Si. Analysis from the equivalent circuit models confirms the
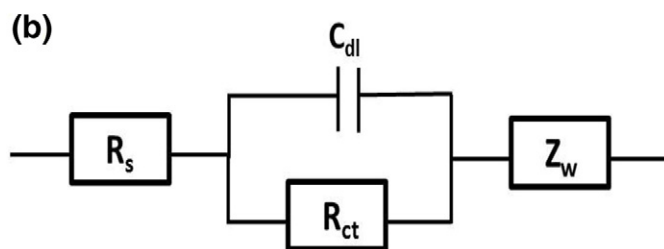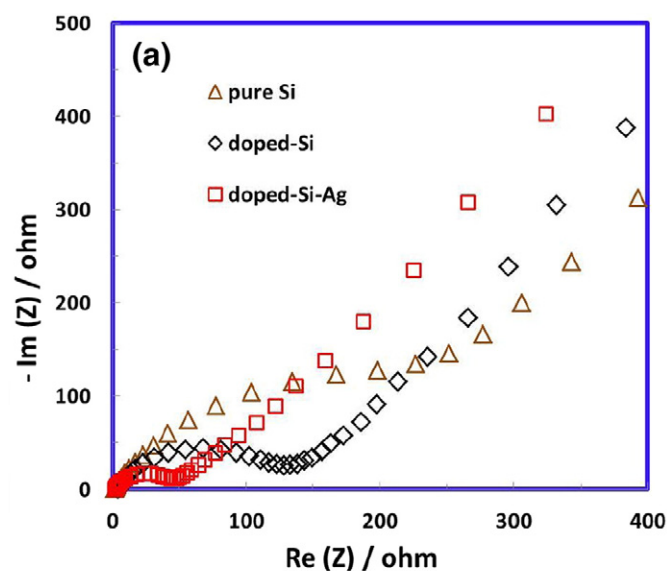
Fig. 1. (a) Electrochemical impedance spectra of the electrodes (i) pure Si, (ii) doped-Si, and (iii) doped-Si–Ag composite before cycling. (b) Equivalent circuit model used to fit the impedance spectra shown in Fig. 1(a).