



Factors influencing cycle-life of full Li-ion cell built from Si/C composite as anode and conventional cathodic material



Krzysztof Kierzek*, Jacek Machnikowski

Wroclaw University of Technology, Faculty of Chemistry, Department of Polymer and Carbonaceous Materials, Gdanska 7/9, 50-344 Wroclaw, Poland

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ABSTRACT

Practical aspects of silicon-based Li-ion battery manufacturing have been discussed in this work. The specially designed T-type full-cell was assembled using the laboratory-made Si/C composite as anodic and commercial LiNiCoMnO₂ as cathodic materials. When cycled in a half-cell with the fixed potential range the Si/C-based anode showed high and stable reversible capacity of about 600 mAh g⁻¹ and low irreversible capacity, below 100 mAh g⁻¹. Advanced tests, performed at various cathode/anode mass ratios with simultaneous monitoring of individual electrode potentials, showed that the perfect cycling stability measured for half-cell cannot be achieved in the real battery configuration. A non-coherent coulombic efficiencies of anode and cathode were pointed out as a main reason of fast capacity decay. Several practical aspects of the Si/C-based Li-ion system, like rate capability and long-term cycleability, were estimated in the prototype CR2032 battery of nominal capacity of 50mAh and compared to the commercial graphite-based cell.

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1. Introduction

The first Li-ion cell was introduced in the market by Sony Corporation in 1991. Since then the capacity of the industrial cell of the same size has grown, approximately, by 10% annually [1] and currently Li-ion system seems to be the best choice for powering all new electronic devices, like smartphones and ultra-light laptops. The increase in energy density is achieved by improving the cell construction as well as by enhancing specific capacity of active electrode materials. Today, the capacity of commonly used cathodic materials (positive electrode) is 140–170 mAh g⁻¹ and due to “open” chemistry can easily increase up to 280 mAh g⁻¹ [2] but it is often associated with higher price of the final product, lower cycling stability and problem with the safety of the battery usage. The improvement of negative electrode is more problematic. The capacity of graphite, commonly used anodic material, is limited to 372 mAh g⁻¹, corresponding to stoichiometric compound LiC₆. Substituting graphite by disordered carbons, thanks to non-stoichiometric lithium accumulation inside the structural defects, can give the capacity of 500 mAh g⁻¹, but with several serious drawbacks [3]. There are several metals, like Si, Sn, Sb, which can be electrochemically alloyed with Li in stoichiometric ratio. The most promising is silicon of huge theoretical capacity

around 4200 mAh g⁻¹, corresponding to Li₂₂Si₅ [4]. However, the application of pure silicon as anodic material is impossible because of poor electric conductivity and huge swelling during lithiation (up to 300%), resulting in low cycle-life of the anode. For these reasons, many researcher propose preparation of high capacity anode based on composite of silicon nanoparticles in a carbon matrix. The role of carbon phase is to facilitate electron transfer to Si particles and to accommodate the local mechanical stress related with silicon expansion [5–9].

In our earlier work we reported on the synthesis and electrochemical performance of Si/C composite prepared from cheap and easily available raw materials by facile and ready to scaling-up synthesis method [10]. The protocol consisted of short milling of micro-sized silicon with toluene suspension/solution of coal-tar pitch, admixing the graphite powder, co-pyrolysis and final heat-treatment at 1100 °C. The specific structure and morphology of the final Si/C powder allowed to prepare an electrode with relatively low amount of binder (15 wt.% of carboxymethylcellulose, CMC and styrene-butadiene rubber, SBR) and conductive additive (5 wt.% of carbon black). Testing of the anode with 10% of Si in a half-cell with metallic lithium as a counter and reference electrode showed reversible capacity above 600 mAh g⁻¹ (per active material), irreversible capacity (below 100 mAh g⁻¹) and the average capacity decay about 0.3% per cycle only. Moreover, due to high packing density of anodic mass (1.35 g cm⁻³), the volumetric capacity of the film exceeded that of industrial graphite anodes by about 10%. The very promising

* Corresponding author. Tel.: +4871 3206506; fax: +4871 3206506.
 E-mail address: krzysztof.kierzek@pwr.edu.pl (K. Kierzek).

performance was achieved using conventional galvanostatic charging/discharging between 1.5 V and 5 mV vs. Li/Li⁺ but without applying artificial electrochemical procedure, e.g. constant capacity discharging [11–13]. Such a procedure extends the cycling-life of the anode but is not acceptable in practical applications.

The specific capacity and stability of Si-based anode is strongly dependent on the potential regime applied [16]. In the full cell, the working potential window of anode, is influenced by many factors, including the mass ratio of cathode to anode, depth of charge, current load, temperature etc. Hence the performance of silicon-based anodes is difficult to predict based on half-cell measurements only.

Within this context, the present work has been focused on the evaluation of the performance of our Si/C composite anode in a full-cell assembled with commercial cathode. We assumed that the reversible capacity C_{rev} of anode should be at least 600 mAh g⁻¹ so to assure acceptable capacity of the final battery. The full-cell capacity as well as anode potential were continuously monitored during charging/discharging of cells with different cathode/anode mass ratios to select optimal configuration. The performance of the Si/C composite was compared to that recorded for the conventional graphite anode.

2. Experimental section

2.1. Si/C composite preparation

The raw materials used for Si/C composite preparation were: silicon powder (Aldrich) with a particle size below 78 μm (325 mesh), battery-grade synthetic graphite powder (TIMREX[®] SLP30, Timcal) and special, particulate matter-free coal-tar pitch of softening point 97 °C (Mettler) and low heteroatom content. Si/C powders (<63 μm) with similar pitch coke contribution of about 17 wt% but various silicon (12 or 18 wt.%) and graphite (71 or 65 wt.%) contents were prepared according to the protocol described in our earlier work [10]. The composites were named 12Si/C (12% of Si) and 18Si/C (18% of Si).

2.2. Anode preparation

A series of electrodes was prepared with 80 wt% Si/C composite, 5 wt% carbon black of high aggregation degree (C-ENERGY[™] SUPER

C65, Timcal), 12 wt% sodium salt of carboxymethylcellulose (Na-CMC, MW ~700 000, Aldrich) and 3 wt% styrene-butadiene-rubber (SBR, MTI Corp., USA) using the following protocol. A slurry obtained by mixing the Si/C composite and carbon black C65 with a water suspension of CMC/SBR and small amount of non-ionic surfactant (Tween 20, Aldrich) was cast on battery-grade copper foil (Schlenk, Germany, 25 μm) used as a current collector. The solvent was evaporated at 120 °C under vacuum overnight and then the film was press-rolled to 30% of the initial film thickness. The final film thickness was in the range of 60–70 μm excluding the current collector. Anodes with a diameter of 12 mm were punched-out, dried under vacuum and introduced in an argon filled glove-box.

For comparison, we prepared anodes with pure graphite (TIMREX[®] SLP30, Timcal) as an active material. In this case, polyvinylidene difluoride (PVDF) was a binder (10 wt.%).

2.3. Cathode preparation

LiNiCoMnO₂ (NMC, atomic ratio of 5:2:3, MTI Corporation) was used as cathodic active material. To prepare the cathode, the slurry of NMC, PVDF (Solef 5130, Solvay) as a binder and carbon black C65 in N-methylpyrrolidone was coated on the aluminum foil (14 μm) and dried. The film consisting of 85 wt.% of cathodic material, 5 wt.% of C65 and 10 wt.% PVDF was press-rolled to the level of 60%. The final thickness was in the wider range of 80–120 μm to cover a demand for appropriate cathode/anode mass ratio.

2.4. Electrochemical measurements

Preliminary tests to assess the impact of discharge cut-off potential on Si/C performance were carried out in simple coin-type cells (CR2032, Hohsen Corp., Japan). Composite anode was working electrode and metallic lithium foil as counter and reference electrode.

Advanced electrochemical study was performed in 3-electrode Swagelok-type cell (T-cell) of perfluoroalkoxy (PFA) body and stainless steel connectors (Fig. 1). Testing of cells with different cathode/anode mass ratios included monitoring of cell voltage, potential profiles of electrodes, capacity and anode potential limits during cycling. T-cell was assembled with Si/C composite anode

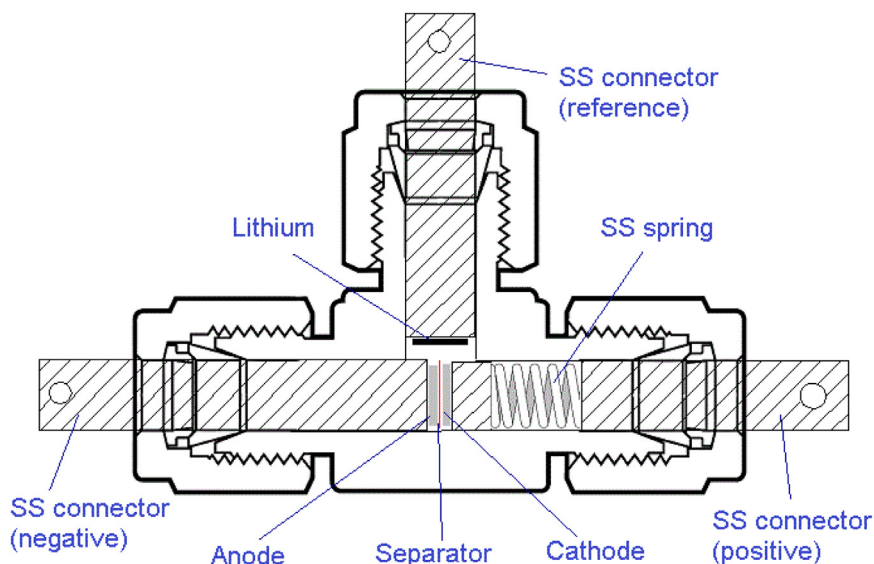


Fig. 1. Schematic of 3-electrode Swagelok cell (T-cell).

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