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Asymmetric Membranes Containing Micron-Size Silicon for High Performance Lithium Ion Battery Anode

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ABSTRACT

Micron-size Si anode is notorious for having extremely poor cycle life. It is mainly caused by the large volume change (~300%) and poor mechanical strength of the Si electrode. Satisfying methods to address this issue are seriously lacking in literature. In this study, novel single-layer, double-layer and triple-layer asymmetric membranes containing micron-size silicon have been fabricated using a simple phase inversion method to dramatically improve its cyclability. The electrochemical performance of these asymmetric membranes as lithium ion battery anodes are evaluated and compared to pure micron-size Si powders and carbonaceous asymmetric membranes. All three types of asymmetric membrane electrodes demonstrate significantly enhanced stability as compared to pure Si powders. The single-layer asymmetric membrane has the largest capacity degradation due to the loss of pulverized Si powders from the membrane surface, only 40% of whose capacity can be retained in 100 cycles. But this performance is still much better than pure micron-size silicon electrode. After being coated with nanoporous carbonaceous layers on both sides of a single-layer asymmetric membrane to make a triple-layer asymmetric membrane (sandwich structure), the capacity retention is notably increased to 88% in 100 cycles at 610 mAh g^{-1} and 0.5C. The enhanced stability is attributed to the extra nanoporous coatings that can prevent the fractured Si powders from being leached out and allow facile lithium ion diffusions. Such a novel, efficient and scalable method may provide beneficiary guidance for designing high capacity lithium ion battery anodes with large volume change issues.

1. Introduction

Lithium Ion Battery (LIB) is deemed as one of the most important power sources for mobile electronics, electric vehicles, and large scale static electricity storage due to its light weight, high energy density and long cycle life [1,2]. Although commercial graphite anodes have an excellent cycling life, they do suffer from an intrinsically low capacity (372 mAh g^{-1}) [2,3]. In contrast, silicon (Si) as an alloying electrode material for LIB possesses an extremely high theoretical capacity (4200 mAh g^{-1} based on $Li_{22}Si_5$). Furthermore, its abundance in the earth's crust is very rich (~28 wt. %), thus bearing a great potential to replace graphite anode for next-generation high capacity LIBs. However, its poor mechanical strength and large volume variation (~300%) during Si alloying and de-alloying processes can lead to fast electrode pulverization, loose contact with conductive additives and rapidly fading capacity [2,4,5]. In addition, the fractured silicon can consume extra amounts of electrolytes causing excessive solid electrolyte interphase (SEI) growth and resulting in a low coulombic efficiency [6].

Innovative strategies have been proposed to tame the aforementioned problems of Si anodes, most of which are associated with various kinds of nanostructurings including nanoparticles (NPs), nanowires (NWs), nanotubes (NTs), nanofibers (NFs), nanoscale thin films, mesoporous and microporous materials [3,4,7–10]. Small dimensions of Si nanomaterials can dramatically reduce the lithium-ion diffusion length and thus benefit a high rate performance, considering that lithium ions have a much lower diffusion coefficient in silicon as compared to graphite (~10^{-10} vs. 10^{-6} cm^2 s^{-1}) [11]. In addition, Si NPs can better withstand the lithiation and de-lithiation process without being significantly cracked [12]. Unfortunately, the current fabrication cost of Si NPs can be more than one order of magnitude higher than that of Si micron-size powders (Si MPs) [13]. Thereby it is economically more profitable to use Si MPs instead of Si NPs for LIB anodes. Also Si MPs have a much higher tapped density than Si NPs [14,15]. But the cyclability of Si MPs-based anode is extremely unsatisfying as evident by nearly total capacity loss in as few as 5

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cycles [15,16]. Recently, it was reported that the mixture of Si NPs and Si MPs can be cycled for 30 times with 75% capacity retention [16]. Cui's group synthesized novel self-healing polymers with low T_g temperatures to fill the gaps between fractured Si micron-powders, resulting in a much enhanced stability (~90% capacity retention after 100 cycles) [17]. But all these reported methods are either low in efficiency, expensive to manufacture or difficult to scale up. Current research lacks an efficient way to fabricate Si MPs-based LIB anodes with a satisfying cycle life using a highly scalable method, e.g. roll-to-roll continuous processing technology.

Polymeric asymmetric membranes like reverse osmosis (RO) and nanofiltration (NF) membranes have been widely used in water desalination and purification, which are commercially available and can be produced on a large scale using a roll-to-roll coating method [18]. Typical asymmetric membranes prepared using a so-called phase inversion method consists of a nanoporous skin layer supported by a macroporous underlying layer [19]. Most recently, our laboratory reported that the capacity retention of single-layer asymmetric membrane containing micron-size Ge can be moderately improved to ~70% after 100 cycles [20]. However, the price of germanium is orders of magnitudes higher than that of silicon, thus seriously limiting its practical applications. Initially, our laboratory tried to fabricate single-layer asymmetric membranes containing micron-size Si using the same technology as the one for single-layer asymmetric membranes containing micron-size Ge. But the cycling performance of single-layer asymmetric membrane containing micron-size Si is still poor (~40% capacity retention after 100 cycles as reported in this study) because Si has a much higher tendency to crack during repeating lithiation/de-lithiation than micron-size Ge as revealed by *in situ* TEM studies from Cui's group [21,22]. Thereby double-layer and triple-layer (sandwich) asymmetric membranes containing micron-size Si are proposed to dramatically enhance the cycle life. We demonstrate that the extra asymmetric membrane coating(s) containing NO silicon on the top of the single-layer Si asymmetric membrane can efficiently reduce the loss of active material Si MPs, resulting in much improved electrode stability. The unique triple-layer sandwich membrane structure has never been reported, thus making this study distinguished from all previous works.

The Si MPs-based triple-layer (sandwich) asymmetric membrane electrode exhibits the highest stability with 88% capacity retention after 100 cycles at ~0.5C. 74% capacity can be retained when the C-rate is increased from 0.05 to 0.5C (820 vs. 610 mAh g^{-1}), which is nearly double that of commercial graphite anode materials. This important method differs from other relative works in many respects, e.g. low fabrication cost (using Si MPs), outstanding cyclability, high scalability, self-assembly manufacturing process and novel triple-layer sandwich asymmetric membrane structure.

2. Experimental

2.1. Synthesis of single-layer asymmetric membranes containing micron-size silicon

First, 0.75 g of polyacrylonitrile (PAN) (M_n = 150,000; Pfaltz & Bauer) was dissolved in 11 mL N-methyl-2-pyrrolidone (NMP) (Sigma Aldrich, >99.5%) using a sonic bath (Bransonic CPX3800H) for 1 hr. Next, 0.25 g of as-received Si powder (American Elements, ~1 μm, S1) and 0.20 g carbon black (CB, TIMCAL SUPER C45 with a surface area of 45 $m^2 g^{-1}$) were added to the solution and dispersed using a sonic bath for 2 hrs. After sonication, the homogenous solution was then coated onto a silicon (100) wafer (2 in. diameter) using a doctor blade set to deliver a wet coating thickness of 100 μm. Next, the coated wafer was immersed in deionized water for phase inversion. The membrane was left in DI water for 30 minutes and then placed in ethanol for another 30 minutes to remove residual moisture. It is noteworthy that the moisture may lead to the oxidation of silicon powders at high temperature during the carbonization process. Finally, the membrane was carbonized at 800 °C for 2 hrs in a tube furnace (Lindberg/Blue M™ 1100 °C) and under the protection of helium gas (99.9999%, Airgas He UHP300) with a flow rate of 200 sccm. The temperature was ramped at rate of ~60 °C min^{-1}. These membranes are labeled PAN/Si herein.

2.2. Synthesis of double-layer asymmetric membranes containing micron-size silicon

A mixture of 0.75 g of cellulose acetate propionate (M_n = 15,000; Acros) and 0.2 g of carbon black was dispersed in 5 mL of acetone using a sonic bath for 1 hr. This mixture was then coated on the top of the un-carbonized PAN/Si membrane using a doctor blade set to ~25 μm. Next, the coated membrane was placed into ice cold ether (ACS Grade, EMD Millipore Corporation) for phase inversion to generate a double-layer asymmetric membrane. Lastly, the membrane was carbonized at 800 °C for 2 hrs in a tube furnace and labeled as CA/PAN/Si herein.

2.3. Synthesis of triple-layer sandwich asymmetric membranes containing micron-size silicon

First, 1.2 g of cellulose acetate and 0.4 g carbon black were dispersed in 15 mL acetone to make a suspension. Next, an un-carbonized PAN/Si asymmetric membrane was dipped directly into the suspension and then slowly withdrawn out of the suspension. In the next step, the dip-coated membrane was immersed into ice cold ether to form a triple-layer sandwich asymmetric membrane. Similarly, the triple-layer sandwich asymmetric membrane was carbonized at 800 °C for 2 hrs in a tube furnace and labeled CA/PAN/Si/CA.

2.4. Synthesis of asymmetric membranes without silicon for control

Asymmetric membranes containing no Si MPs were also prepared using the aforementioned method for control experiments. The membranes were carbonized at 800 °C for 2 hours and labeled as PAN.

2.5. Characterization

A field emission scanning electron microscope (JEOL JSM-7600F) equipped with a transmission electron detector (TED) was used for morphology and structure characterizations. Raman studies were carried out using a ThermoScientific DXR SmartRaman Spectrometer with a 10× lens magnification, 150 second collection time, a 1 mW laser of 532 nm, and a 50 μm slit aperture. Phase identification was performed using a powder X-ray diffractometer (Rigaku MiniFlex 600) at Armstrong State University. The samples were scanned using Cu Kα (λ=0.1542 nm) radiation with a step rate of 0.2° per second from 10–90° (2θ). The silicon content was determined using a thermogravimetric analyzer (TA Instruments G50 TGA). Compressed air (Ultra Zero, Airgas) with a flow rate of 20 mL min^{-1} was used as the purging gas. The temperature was ramped from room temperature to 700 °C at a rate of 10 °C min^{-1}. Surface area and pore size distribution experiments were completed on a Micrometrics ASAP 2020 Surface Area and Porosity Analyzer. The surface area was calculated using Brunauer-Emmett-Teller (BET) equation and pore size distribution was determined using the Barrett-Joyner-Halenda (BJH) method. Samples were degassed at 50 μTorr for 300 °C for