High-Energy-Density and Low-Cost Lithium-Ion Batteries Using Sulfurized Polyacrylonitrile Cathodes

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Abstract: The paper presents preliminary results on a novel high-energy lithium-ion-battery (LIB), in which the sulfur-polyacrylonitrile (S-PAN) is cathode material, the micro silicon oxide (SiO_x) is anode material, and pre-lithiation technique is utilized to introduce lithium (Li) into the battery in order to match the electrode capacity and also to compensate for the initial Li loss of SiO_x anode. In this novel battery structure, high sulfur weight ratio in S-PAN is prepared by heat treating sulfur and long chain PAN under inert gas to achieve a specific capacity above 650 mAh/g. The specific capacity of SiO_x is over 700 mAh/g. The specific energy of the new LIB can exceed the current LIBs.

Keywords: Lithium-ion batteries, sulfurized polyacrylonitrile, graphite, silicon/carbon

Introduction

With the global push toward green energy, researchers world-wide are pursuing the development of low-cost, high-energy-density, long-life rechargeable battery technologies to be used in many civilian and military applications. Achievement of a specific energy (e.g. >500 Wh/kg), a cycle life (e.g. >1,000 cycles), and a cost (e.g. < $100/kWh) has become a technical target adopted by many major industrial countries. We have developed a novel approach to fabricate high-specific and low-cost LIBs using sulfurized polyacrylonitrile (S-PAN) as cathode, graphite or silicon-carbon (Si/C) as anode, and pre-lithiation technique to introduce required lithium-ion.

Specific Energy

The ultimate specific energy based on active electrode materials only in a LIB can be expressed as:

$$E = V \left(\frac{1}{c_a} + \frac{1}{c_c} \right)^{-1} \tag{1}$$

where c_a and c_c are the specific capacities of anode and cathode, respectively; V is the average cell voltage. In amount of cathode materials, we chose $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ (NCM333) having the highest specific capacity of 220 mAh/g as an example [1]. Fig. 1 shows the specific energy of a LIB (blue line) using NCM333 as a function of specific capacity od anode. The average cell voltage of 3.7 V was used. It can be seen that the specific energy is from 525 Wh/kg (c_a=372 mAh/g for graphite), increases to 685 Wh/kg (c_a=1,000 mAh/g for Si-carbon) and 791 Wh/kg (c_a=3,860 mAh/g for Li metal). The specific energy increases 28% when the specific capacity of anode increases 2.7 times (from 372 to 1,000 mAh/g), and increases only 15% when the specific capacity of anode increases another 3.8 times (from 1,000 to 3,860 mAh/g). It is because that the reciprocal of the effective specific capacity of the cell is the sum of reciprocal of the specific capacity of the anode and cathode electrodes as shown in Eq. (1); therefore, among the two electrodes, the electrode with the smaller specific capacity will play a predominating role in determining the final specific energy of the cell. One of the big challenges for developing high-energy LIBs is that so far, a high-capacity cathode material matching the high-capacity metal Li or Si-C anode, has not yet been found. The specific energy formula tells us that when the specific capacity of the cathode electrode and the anode electrode are both large, it will be a more effective way to increase the specific energy of the battery. Looking at the currently known electrode materials in Li system, sulfur and Si-carbon composite become candidates as cathode and anode materials for high-energy batteries.

With developed S-PAN cathode, SiO_x anode, and pre-lithiation techniques, the high specific energy cell can be built. The specific energy based on active materials (cathode, anode, and extra Li source for pre-lithiation) is calculated and shown in Fig. 1 as orange line using the following equation [2].

$$E' = V \left(\frac{1}{c_a} + \frac{1}{c_c} + \frac{1}{c_{Li}} \right)^{-1} \tag{2}$$

where, c_{Li}=3,860 mAh/g is the specific capacity of Li metal. From Fig. 1, it can be seen that when the specific capacity of anode is less than 1050 mAh/g, the specific energy of conventional LIB is greater than that using S-PAN due to low cell voltage (1.9 V); however, the increase rate of specific energy is greater than that for conventional LIB. When the specific capacity of anode is 1,200 mAh/g, the specific energies are 706 Wh/kg vs. 722 Wh/kg for LIB using NCM and S-PAN cathodes, respectively. From the preliminary simulation results as shown in Fig. 1, we can conclude that using a high-capacity but

low-potential S-PAN is more likely to achieve a specific energy exceeding 500 Wh than using any lithium-metal-oxide as a cathode to combine with a high-capacity anode to form a LIB. Although lithium-metal-oxide has a higher potential, the specific capacity is not satisfactory and is much less than that of S-PAN. The highest specific capacity of S-PAN at 900 mAh/g was reported [3].
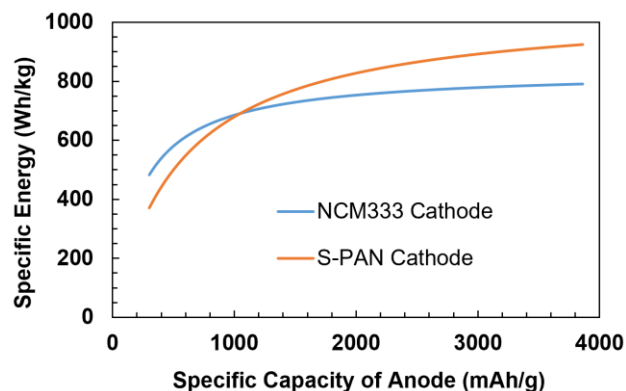

Fig. 1 Specific energy of proposed LIB using S-PAN cathode and LIB using NCM333 cathode based on active materials only including anode, cathode, and Li source for LIB using S-PAN. The specific capacities of 222 and 650 mAh/g are used for NCM333 and S-PAN cathodes, respectively. The cell voltages of 3.7 and 1.9 are used for cells used NCM333 and S-PAN cathodes, respectively.

Experimental
S-PAN was prepared by mixing sulfur (Sigma-Aldrich) and polyacrylonitrile (Sigma-Aldrich) at a weight ratio of 4:1, and then heating the mixture at 350 °C for 3 hours in a nitrogen atmosphere to form the S-PAN composite material, and S-PAN powders were obtained by grinding in a mortar and pestle for 30 minutes.

The cathode was made by mixing 80 wt% S-PAN powders, 10 wt% Super P C65, and 10 wt% styrene-butadiene rubber/carboxymethylcellulose (SBR/CMC) binder, then the mixture was dispersed in water to form the slurry. The well-mixed slurry was cast by using a doctor blade on aluminum foil as current collector. After drying at room temperature, the electrodes were dried again in a vacuum oven at 70 °C for 12 h to remove moisture. Then the cathodes were cut to ½ inch diameter discs. The typical cathode loading was about 8 mg/cm^2.

The anode was made with SiO_x and graphite powders as active materials. the anodes were cut to ½ inch diameter discs and dried at 90 °C in vacuum oven for 12 h. During the assembly of the cell, a 20 μm-thick Li foil is pressed on the surface of the anode or cathode as the pre-lithiation source. The size of Li foil

was determined such that the Li capacity was equal to the sum of the capacity of the anode and the irreversible capacity of the cathode during the initial cycle.

The coin cells were assembled in an Argon filled glove box. Three different kinds of coin cells were assembled including 1) Li/S-PAN half-cells, 2) Li/SiO_x-graphite half-cells, and 3) SiO_x-graphite/S-PAN full-cells. In all cells, the separator was Celgard 2400. The electrolyte was LP40 (1 M $LiPF_6$, ethylene carbonate (EC)/diethyl carbonate (DEC)=1:1). After SiO_x-graphite/S-PAN full-cells were assembled, we waited for 270 h for pre-lithiation before any characterization.

The galvanostatic discharge/charge for assembled cells in voltage ranges of 1.0-3.0 V for Li/S-PAN, 0.01-1 V for Li/SiO_x-graphite, and 0.01-3 V for SiO_x-graphite/S-PAN were tested by using a battery tester (Neware).

The electrode morphology, particle size, and elemental mapping were observed by a field emission scanning electron microscopy (FE-SEM) using a Carl Zeiss AURIGA CrossBeam. The elemental mapping was studied with an IXRF energy dispersive X-ray spectrometer (EDS) using a Hitachi S4000.

Results and Discussion
Fig. 2 shows (a) the voltage profile of initial cycle and (b) specific capacity capacities and Coulombic efficiency as a function of cycle number from a Li/S-PAN half-cell. It can be seen that the specific capacity of the 2nd cycle decreased from 789 mAh/g in the 1st cycle to 654 mAh/g, a loss of 20%; however, after the 1st cycle, the decay of the specific capacity of the S-PAN cathode is less than 2% per cycle in the next more than 40 cycles. It can also be seen from Fig. (a) that the potential of the S-PAN cathode in the 1st discharge was about 0.2 V lower than that in the 2nd cycle and could be due to solid electrolyte interface layer formation, S-S and C-S bonds broken [4]. After the 1st cycle, the potential of S-PAN cathode is stable. From Fig. 2(c), the S-PAN cathode capacity exhibits a sharp drop at 1C rate, in sharp contrast to our previous results [5], in which the loading of S-PAN was roughly half and the weight ratio of carbon in the electrode was more than double. However, further studies are needed to understand the most dominant factors limiting S-PAN cathodes.
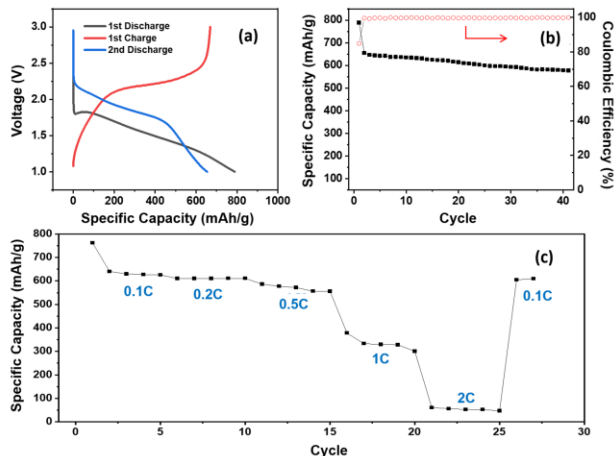
Fig. 2 (a) Voltage profile (b) cycling performance at 0.1C rate, and (c) rate performance of Li/S-PAN cells.

Similar tests were performed on Li/SiOx-graphite half-cells, Fig. 3 shows a comparison of cycling performance of SiOx-graphite and S-PAN during 1st 40 cycles. Different to the S-PAN cathode, the specific capacity of SiOx-graphite anode increased from an initial 600 mAh/g to a maximum of 710 mAh/g, about 18% increase. It is believed that is due to an activated process that because low current density could form more irreversible conductive Li4SiO4 and Li2O to increase the electrode Li-ion conductivity [6]. In order to fully activate the SiOx-graphite anode, during the initial few cycles, the SiOx-graphite anode needs to be cycled at a low rate, such as less than 0.05C rate. After several cycles, both electrodes have good Coulombic efficiencies. It can be seen from Fig. 3 that the capacity decay rate of anode is faster than that of cathode.
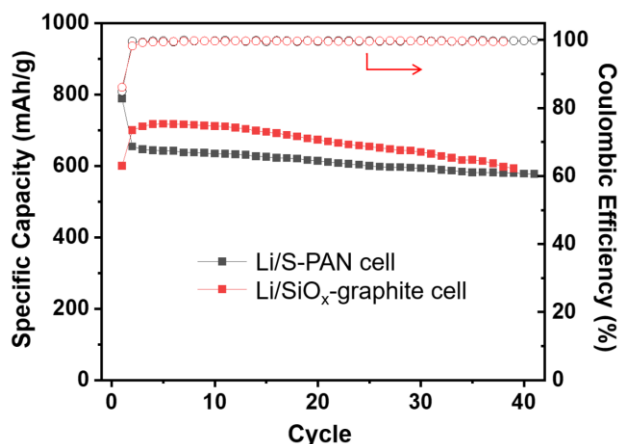

Fig. 3 A comparison of cycling performance of SiOx-graphite and S-PAN. SiOx-graphite was cycled at a rate of 0.05C for the first two cycles and then at a rate of 0.1C.

SiOx-graphite/S-PAN full-cells were assembled with capacities of 6.84 mAh for anode and 8.31 mAh for cathode. The thicknesses of pristine electrodes are 59 μm and 222 μm for anode and cathode, respectively. Both electrode diameter is ½ inch. For SiOx-graphite/S-PAN cells, the pre-lithiation is essential because neither the anode nor the cathode is pre-doped with Li, so all Li sources only enter the anode or cathode through pre-lithiation, in addition, the pre-lithiation can also canoed and compensate for the initial Li loss of S-PAN cathode and SiOx-graphite anode.

Fig. 4 shows performance measured from SiOx-graphite/S-PAN full-cells. From Fig. 1(a), the Coulombic efficiency of the 1st cycle is about 84%. The capacity decayed about 22% during the 1st cycle, then the decay of the cell capacity is about 2.5% per cycle in the next more than 24 cycles as shown in Fig. 4(b). The capacity decay rate of full cell is slightly higher than that of cathode. Fig. 4(c) shows the rate capabilities of the cell from 0.1C to 1C. It can be seen that the capacity drops sharply at the 1C rate, which is consistent with rate performance of S-PAN cathode; therefore, the rate performance of SiOx-graphite/S-PAN cell was limited by slow cathode response.
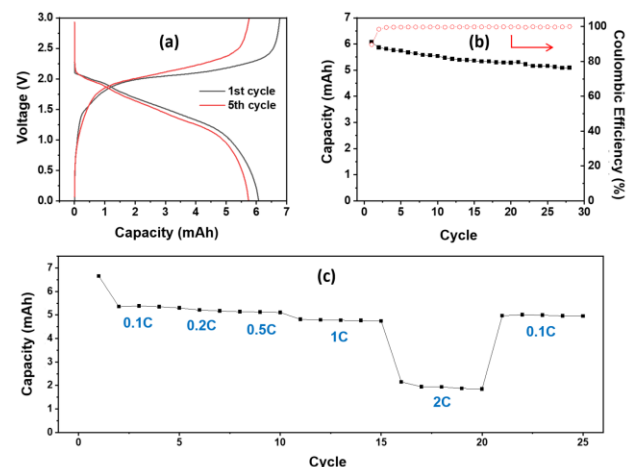

Fig. 4 (a) Voltage profile, (b) cycling performance at 0.1C rate, and (c) rate performance of SiOx-graphite/S-PAN full-cells. The S-PAN cathode was pre-lithiation before the 1st cycle.

Due to high specific capacities of both electrodes, the volume and porosity of the electrodes may change greatly after being fully lithiated. Fig. 5 shows SEM images of S-PAN cathode surface (a) before and (b) after pre-lithiation. It can be seen that the particle size was significantly increased after pre-lithiation. The thickness of the cathode electrode was measured and found to be expanded from 222 μm to 243 μm, before and after pre-lithiation, an increase of about 9.5%. The porosity of cathode was estimated to be 59% and 49% before and after pre-lithiation, respectively.
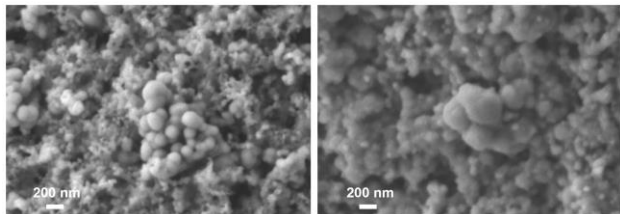
Fig. 5 SEM images of S-PAN cathode surface (a) before and (b) after pre-lithiation.

Fig. 6 shows SEM images of SiOx-graphite anode surface (a) before and (b) after pre-lithiation. The thickness of the anode electrode was found to be expanded from 59 μm to 112 μm before and after pre-lithiation, an increase of about 90%, which is much greater than that obtained from cathode electrode. Unlike the cathode, the porosity of anode increased from 44% of the pristine electrode to 56% after pre-lithiation. It can also be seen from SEM images, the particle size after pre-lithiation became smaller. This is because after the lithiation, a huge volume expansion occurred, leading to severe structural collapse and fragmentation inside the SiOx particles.
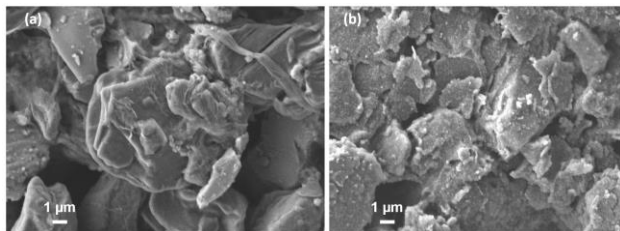

Fig. 6 SEM images of SiOx-graphite anode surface (a) before and (b) after pre-lithiation.

Conclusion
Both electrodes in SiOx-graphite/S-PAN cells are made with low-cost raw materials. In cathode, sulfur is one of the most abundant elements on the Earth and another major material in cathode, PAN is also low in price; in anode, micron-sized SiOx is commercially available on low-cost that is comparable to graphite. Theoretically, the specific energy of LIB using S-PAN based cathode can be greater than that using Li metal oxide based cathode. We have demonstrated that when sulfur is bonded to macromolecular PAN to form S-PAN, soluble lithium polysulfides are not formed during lithiation; thus, S-PAN exhibits good cycle life and high Coulombic efficiency. However, there are still many challenges to make this new battery comparable to existing LIBs, such as improving the rate capability and cyclability of the S-PAN cathode. The large difference in expansion and compression of the S-PAN cathode and SiOx-graphite anode volumes during charge and discharge makes battery packaging and modules very difficult.

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