Polymer Electrolyte for Silicon Anode in Lithium-ion Battery

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Abstract

Lithium-ion battery is an important invention that people use on a daily basis. The increased daily usage and many current researches being made on renewable energy made Li-ion battery performance need to be enhanced as well. Silicon has been regarded as a high-capacity anode for lithium-ion batteries. However, its commercial use has been held back due to is volumetric expansion during cycling. Based on the drawback of silicon anode, a solid polymer electrolyte is made to withstand anode expansion while still has its ability to transfer electron inside battery. 2-Acrylamido-2-methylpropane sulfonic acid (AMPS) and Butyl Acrylate (BA) based polymer is then used as an electrolyte material to provide toughness, ion-conductivity, and self-healing properties.

Introduction

Lithium-ion battery has been widely used as a reliable energy storage. At the same time, modern researches are moving toward renewable energy sources. Solar Radiation, wind, and waves are some sources that are used to be converted into energy. As a dependable energy source compared to fossil fuel, improvement on renewable energy is a popular topic to be researched on. In support of this, energy storage is another aspect that can be improved. Moreover, public preferences became more oriented toward portable devices, as they are more convenient to use on daily basis. As time goes, usage and number of portable devices will increase.[1, 2]

Improvement of lithium-ion battery as an energy storage is highly needed due to increasing energy usage and demand. At present, graphite is used as an anode in lithium-ion batteries. However, it has a quite small theoretical gravimetric capacity of 372mAh g^{-1}. To increase capacity of battery, different anode is selected to replace conventional graphite anode. Silicon has a very high gravimetric capacity of 4200mAh g^{-1}, more than ten times of graphite anode. Despite its high capacity, silicon anode commercial use is hindered by its volumetric expansion during cycling. Mechanical strain from its enormous volumetric expansion leads to crack. In addition, deformation of solid electrolyte interphase (SEI) also occurs due to its expansion.[3]

Modifications of battery components can be made to resolve this problem. For this study, modification of electrolyte is made to withstand the expansion of silicon anode. The modified electrolyte needs to have consideration on its toughness, conductivity, thermal properties, toxicity, while still having a good conductivity.[4] Choosing solid electrolytes over gel and liquid electrolyte eliminates the need of liquid containment, which improve its safety and stability, while having tough properties to withstand expansion of anode.[5] Two general types of material used for polymer electrolytes are ceramic and polymer, both with different mechanical properties. In this study, polymer material is preferred due to its chain flexibility and easy to process while maintaining solid electrolytes properties.

2-acrylamido-2-methylpropane sulfonic acid (AMPS) is remarkably known for its ion-conductivity, self-crosslinking, and self-healing ability. AMPS has been used for polymer electrolytes for its electron withdrawing sulfonate and amide group.[6, 7] Moreover, its self-healing ability arises due to intermolecular hydrogen bonds, acting as physical cross-links.[7, 8] Here, butyl acrylate (BA) is introduced to increase flexibility and chain mobility, thus improving ion conductivity.[9]

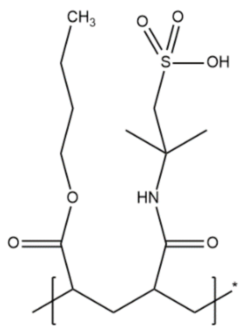

Figure 1. Structure of p($AMPS_m$-*co*-BA_n)

Motivation

The usage and demand for energy storage has been increasing for the last decade. Silicon anode is one of the great answers to enhance the capacity of Li-ion battery. Silicon anode provides 10 times larger capacity than conventional graphite anode. Its volumetric expansion, however, is a problem that is hard to solve. By researching on its solution, a breakthrough might be made for future uses. Polymer-based solid electrolyte has a lot of advantages compared to other solutions. It is cheap, easier to process, and also safe. By completing this research, it is hoped that will be a great breakthrough to enhance the performance of Li-ion battery.

Description of Research Work

Synthesizing p($AMPS_m$-*co*-BA_n)

p($AMPS_m$-*co*-BA_n) was synthesized via free radical polymerization at different molar ratios. Polymerization was done in mole ratios of 1:9, 2:8, 3:7, and 4:6 (with m and n are AMPS and BA ratios respectively). In this experiment, AIBN was chosen as initiator. The monomer to initiator ratio used in this experiment was 250:1, with 35mmol of total used monomer. At the start of the process, measured amount of BA was mixed with methanol(35ml) inside round bottom flask(stirrer included) and purged under Ar condition while stirring (300-350rpm). Solid AMPS and AIBN then put into inside Schlenk flask(stirrer included) and alternately put under vacuum and Ar condition to remove excess oxygen for around 45 minutes(vacuum starts for 15 minutes, followed by Ar 5 minutes, vacuum 10 minutes, Ar 5 minutes, vacuum 5 minutes, Ar 5 minutes). BA mixture then carefully put into Schlenk flask containing AMPS and BA, stirred at 1150rpm and heated in 65^{o}C temperature for 24 hours. After polymerization, purification process is done by dialysis against methanol to remove excess unreacted monomer.

Results and Discussion

Nuclear Magnetic Resonance (NMR) test was done to identify the structure of synthesized p($AMPS_m$-*co*-BA_n).

c)

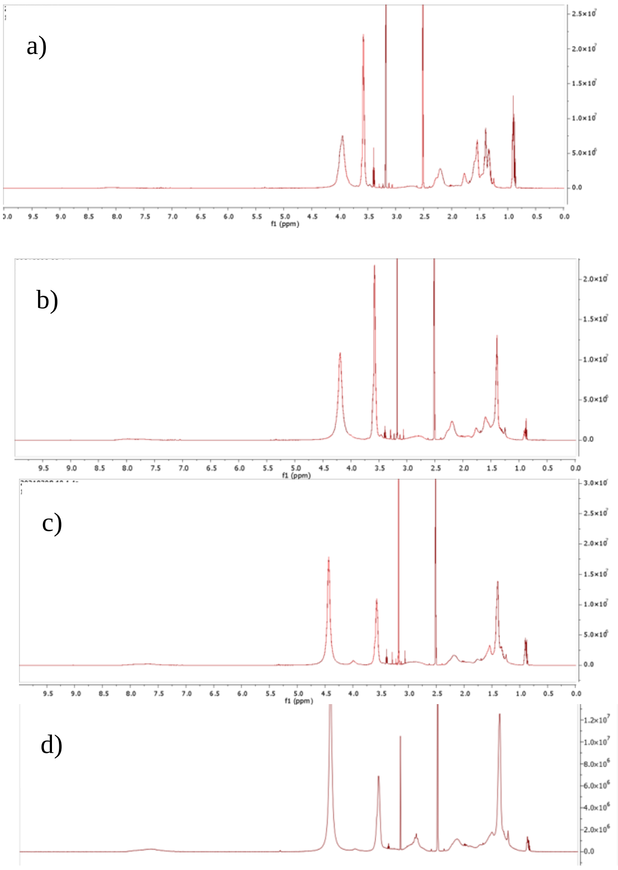

Figure 2. NMR test result of (a) p($AMPS_1$-*co*-BA_9). (b) p($AMPS_2$-*co*-BA_8). (c) p($AMPS_3$-*co*-BA_7). (d) p($AMPS_4$-*co*-BA_6).

Results of the test show desired structures of p($AMPS_m$-*co*-BA_n) in all ratios. -CH3 and -CH2 of Butyl acrylate are represented by peaks around 0.9ppm-1.75ppm, while -NH peak of AMPS is represented by small broad peak in 7.0ppm-8.5ppm.

In addition to NMR test, Gel Permeation Chromatography (GPC) was done to analyze molecular weight and polydispersity of synthesized polymer. GPC test was done with dimethylformamide (DMF) as solvent.

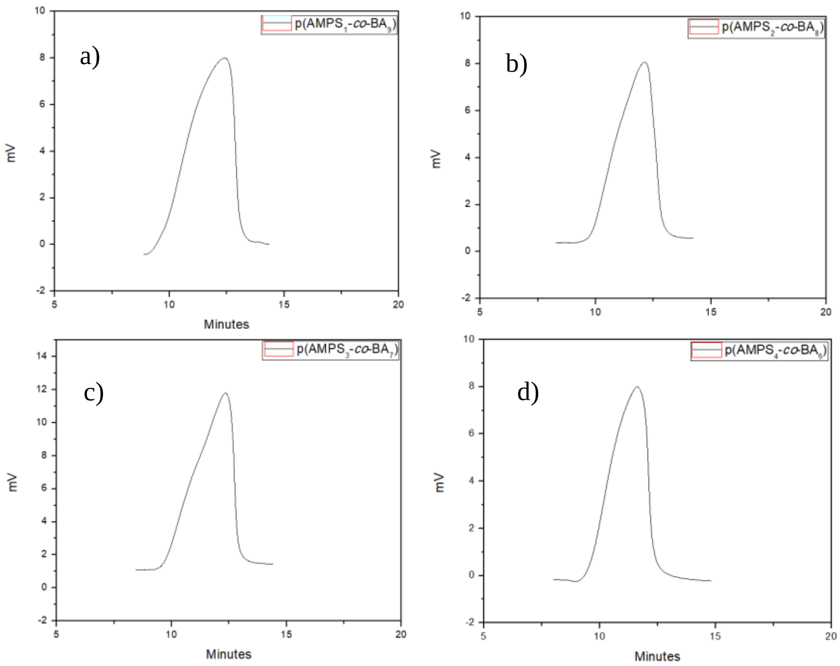

Figure 3. GPC test result of (a) p($AMPS_1$-*co*-BA_9). (b) p($AMPS_2$-*co*-BA_8). (c) p($AMPS_3$-*co*-BA_7). (d) p($AMPS_4$-*co*-BA_6).

Polymer Ratio	p($AMPS_1$-*co*-BA_9)	p($AMPS_2$-*co*-BA_8)	p($AMPS_3$-*co*-BA_7)	p($AMPS_4$-*co*-BA_6)
Weight average molecular weight (Mw)	1,161,894	1,177,917	1,142,052	1,500,229
Number average molecular weight (Mn)	888,757	974,392	915,378	1,300,502
Polydispersity (PDI)	1.3073	1.2088	1.2476	1.1536

Table 1. Weight average molecular weight and number average molecular weight based on GPC test result of p(AMPS-*co*-BA)

The result gained from GPC shows very high value of molecular weight, for both weight average molecular weight and number average molecular weight. High number of test result were speculated to be machine error. To prove this speculation, a GPC test was made using commercial polymer of Polyacrylonitrile with pre-tested average Mw of 150,000.

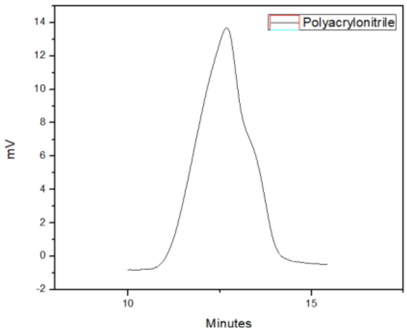

Figure 4. GPC test result of Polyacrylonitrile in purpose of testing GPC machine condition

The result shows Polyacrylonitrile with Mw of 600,366 and Mn of 458,221. Results obtained have huge differences compared to average Mw listed. In conclusion, Mw and Mn results obtained from this GPC test cannot be fully used as a basis for future uses. However, polydispersity result of GPC test may be concluded as close to actual value as both Mw and Mn number rise at same time.

As a solid electrolyte used for silicon anode Li-ion battery application, p($AMPS_m$-*co*-BA_n) is expected to withstand volumetric expansion of silicon during cycling process. On the process, crack and scratches may happen duo to mechanical strain caused by anode. AMPS has the ability to conduct self-healing due to hydrogen bonding by its functional groups. To test self-healing ability of p($AMPS_m$-*co*-BA_n), self-healing test was conducted. The self-healing test also use to find a favorable ratio for p($AMPS_m$-*co*-BA_n) to conduct self-healing (AMPS has molecular group for self-healing while BA is flexible, supporting its ability). The process starts by crosslinking the polymer in 80^oC temperature for 5 hours (polymer is at solid state after crosslink process). Afterward, a scratch is made onto the solid polymer surface using knife. After 12 hours, the solid polymer is observed and compared with previous condition after scratch was made.

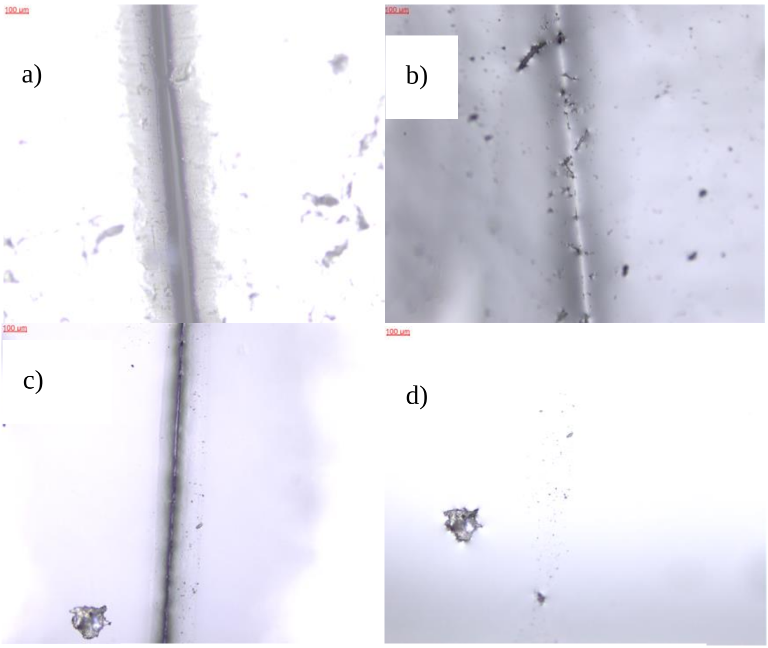

Figure 5. Optical microscope images of (a) p($AMPS_3$-*co*-BA_7) before self-healing. (b) p($AMPS_3$-*co*-BA_7) after self-healing. (c) p($AMPS_4$-*co*-BA_6) before self-healing. (d) p($AMPS_4$-*co*-BA_6) after self-healing

Both p($AMPS_3$-*co*-BA_7) and p($AMPS_4$-*co*-BA_6) are used to test self-healing ability. In this test, optical microscope is used to analyze the condition of polymer after scratch. Both results show the self-healing ability for both ratios. Theoretically, p($AMPS_4$-*co*-BA_6) has much higher self-healing ability compared to p($AMPS_3$-*co*-BA_7) due to larger ratio of AMPS. Experimental results show after 12 hours, p($AMPS_4$-*co*-BA_6) has eliminate the scratch made on its surface while we can see some residues in p($AMPS_3$-*co*-BA_7).

Conclusion

Theoretically, p($AMPS_m$-*co*-BA_n) has all the potential to be the solution of Si anode expansion. Both monomers were known for its properties of ion-conductivity, self-healing, chain mobility, and flexibility. In this work, it is proven that free-radical polymerization can be conducted to synthesize p($AMPS_m$-*co*-BA_n), showed by NMR results given and low polydispersity gained from GPC test. Self-healing test is also conducted to test its ability to self-heal. Two ratios of p($AMPS_m$-*co*-BA_n) are prepared and both shows positive result of its self-healing ability. However, it is too early to conclude the possibility of p($AMPS_m$-*co*-BA_n) to be a good solid electrolyte to be used for silicon anode battery. Experiments, tensile tests, TGA test, and DSC test, is also needed to see its toughness, thermal stability, glass transition temperature, and material properties under high heat. From conductivity point of view, cycling and ion-conductivity test are needed to see its ability to conduct electron and withstand dendrite form after cycling.

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