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]

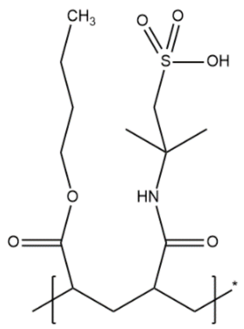


Figure 1. Structure of p(AMPS$_m$-*co*-BA$_n$)

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

From previous section, it is already mention that one of the purpose of AMPS addition is to create self-healing and crosslink ability for the polymer, in which both can happen by presence of sulfonate and amide group. Crosslink process of AMPS is reaction of -OH from each AMPSs molecule that create chemical bond with H_2O as a product. Loss of -OH side group should be noticeable on crosslinked polymer. To prove this, FTIR test was done for each ratio of polymer.

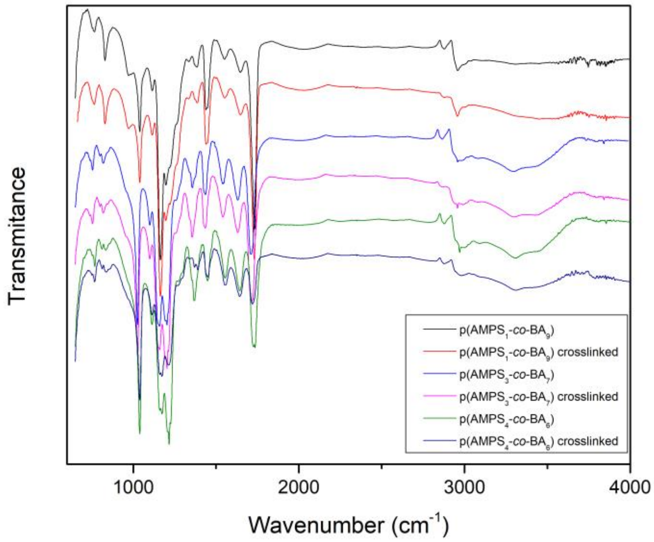


Figure 2. FTIR result of p(AMPS$_1$-*co*-BA$_9$), p(AMPS$_3$-*co*-BA$_7$), p(AMPS$_4$-*co*-BA$_6$), each with before and after crosslinked condition

We can analyze -OH peak from 3000 to 3700 cm^{-1} wavenumber form each ratio. p(AMPS$_1$-*co*-BA$_9$) shows least -OH, and p(AMPS$_4$-*co*-BA$_6$) shows most -OH. This result matches theoretical -OH amount, as it is increases as AMPS ratio increase. -OH side group in can barely be seen due to low AMPS ratio. Moreover, its condition before and after crosslink is also not much different. We can see more -OH side group in p(AMPS$_3$-*co*-BA$_7$) and p(AMPS$_4$-*co*-BA$_6$) on this region. Crosslinked graph of p(AMPS$_3$-*co*-BA$_7$) did not have much difference from before crosslink condition. However, we can see a slight difference in p(AMPS$_4$-*co*-BA$_6$). Crosslink reaction did take place, but on FTIR graph it does not show major difference before and after crosslink.

Designed as a solid electrolyte, p(AMPS$_m$-*co*-BA$_n$) must excel in its mechanical properties compared to gel or liquid electrolyte. Combining both properties of each monomer, it has the advantage of good mechanical strength, flexibility, while also have self-healing ability. For all polymer ratio, tensile test was done to study each mechanical property, the difference of each ratio, and impact given by each type of monomer used.

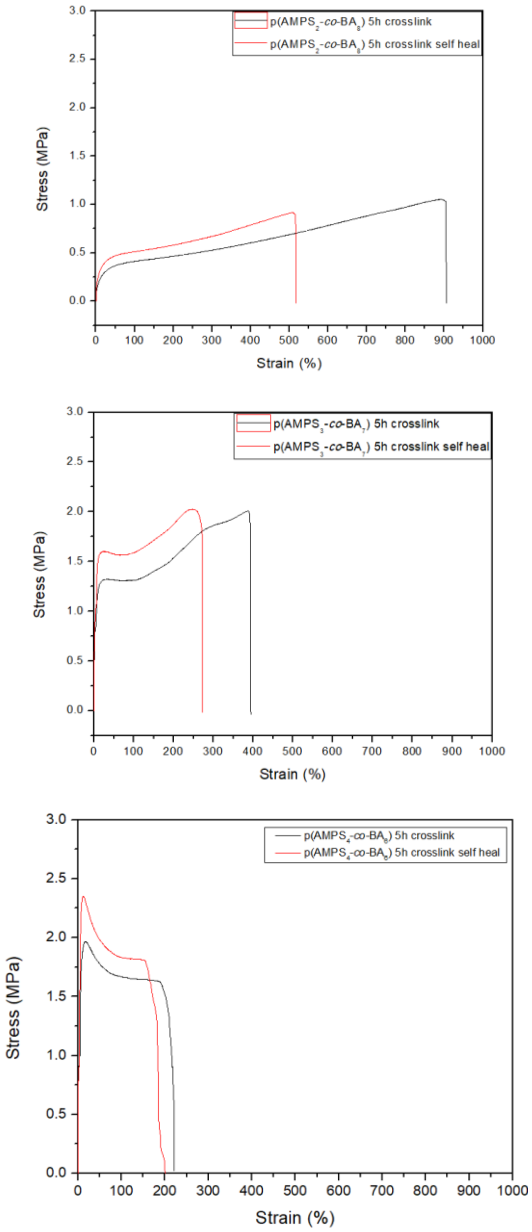


Figure 3. Tensile test result of (a) p($AMPS_2$-*co*-BA_8). (b) p($AMPS_3$-*co*-BA_7). (c) p($AMPS_4$-*co*-BA_6).

At the day of the experiment, an error occurs at measurement preparation of p($AMPS_4$-*co*-BA_6), which interfere the end result of the tensile test. However, we can use this data to compare differences of each ratio, what to expect when increase or decrease each monomer ratio on the polymer.

From tensile test result, we can see the greatest elongation comes from p($AMPS_2$-*co*-BA_8), which extend up to 900% strain for pristine and 500% for self-healed before it breaks. Result from p($AMPS_3$-*co*-BA_7) shows lower elongation at around 400% for pristine and 270% for self-healed before it breaks. p($AMPS_4$-*co*-BA_6) shows the lowest elongation around 200-225% for both pristine and self-healed.

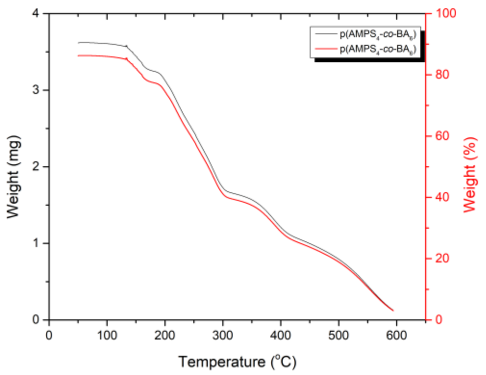
By comparing stress, p($AMPS_4$-*co*-BA_6) shows higher young's modulus compared to other ratio. It also shows little deformation before breaks. p($AMPS_3$-*co*-BA_7) shows lower young's modulus from previous ratio, then goes through deformation while increasing in stress before it breaks. p($AMPS_2$-*co*-BA_8) shows the lowest young modulus before deformation. Same as p($AMPS_3$-*co*-BA_7), its stress increases as the polymer got deformed, then breaks.

It can be concluded that both p($AMPS_4$-*co*-BA_6) and p($AMPS_3$-*co*-BA_7) shows a hard type property. However, p($AMPS_3$-*co*-BA_7) shows better toughness, as it still elongates after deformation starts while increases in stress. p($AMPS_2$-*co*-BA_8) also shows tough properties with the same reason as p($AMPS_3$-*co*-BA_7), but it is softer if we compare to other ratio.

From the result, we can conclude that AMPS affect the toughness of the material, since the higher ratio of AMPS used, the harder the polymer gets. Downside of adding more AMPS is its brittleness the more AMPS ratio is added. BA has a flexible property. In this polymer, BA affects in polymer toughness. By comparing three results, we can see higher toughness in higher BA ratio. However, adding more BA results in soft polymer.

In previous section, p($AMPS_m$-*co*-BA_n) is proposed to be used as electrolyte for battery application. While doing this topic research, I am aware that overheating is one factor that may happen in daily life application. Large electricity draw from a battery can generate heat that can destroy its parts inside. In this research, polymer heat durability must be ensured to withstand heat generated while using.

Polymer state at high heat need to be observed to make sure it can withstand high temperature. Thermogravimetric Analysis (TGA) was done to observe degradation temperature of each polymer ratio.



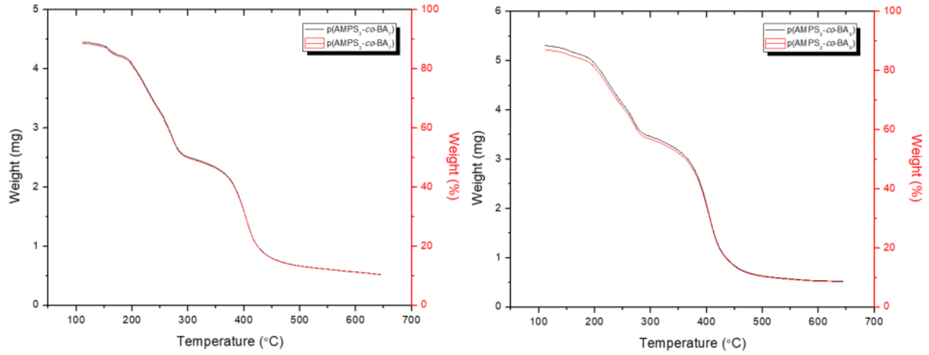


Figure 4. TGA test result of (a) p($AMPS_4$-*co*-BA_6). (b) p($AMPS_3$-*co*-BA_7). (c) p($AMPS_2$-*co*-BA_8).

Observing the result of TGA, p($AMPS_3$-*co*-BA_7) and p($AMPS_2$-*co*-BA_8) ratios both shows similar TGA graph while there are decomposition temperature differences occur in p($AMPS_4$-*co*-BA_6). All three of tested polymer ratio started to decompose at around 200^{o}C. For p($AMPS_3$-*co*-BA_7) and p($AMPS_2$-*co*-BA_8) ratio, decomposition stop at less than 300^{o}C, smaller temperature comparing to p($AMPS_4$-*co*-BA_6) at around 300^{o}C. However, p($AMPS_4$-*co*-BA_6) weight percent decrease at decomposition period has noticeable difference than other ratio tested. Decomposition period lower the weight p($AMPS_4$-*co*-BA_6) to 40% from its initial state. p($AMPS_3$-*co*-BA_7) and p($AMPS_2$-*co*-BA_8) ratio both decompose until weight percentage of around 50-60% from its initial weight.

Conclusion

In conclusion, p($AMPS_m$-*co*-BA_n) can be a good contender for a solid electrolyte to be used on battery application. Looking at its mechanical property, it has hard property and tough at the same time. All sample that are tested did not show any brittle ness to the polymer, meaning it will have its tough property even with increased AMPS ratio. Moreover, all sample tested form tensile test shows self-healing property. It is expected to not become exactly the same with pristine condition, but it still shows hard and toughness, even after being cut. From its thermal analysis aspect, p($AMPS_m$-*co*-BA_n) can withstand up to 200^{o}C from all ratio tested. All ratio mostly losses half of its weight from 200 to 250^{o}C. Based on previous TGA test, thermal property of the polymer can be improved in future research, to find a good point for it to have better thermal property.

In conclusion, It is is very possible for p($AMPS_m$-*co*-BA_n) to be used for battery application, after data that we get from testing its property. Slight improvements can be made regarding its property, but the polymer itself already has needed property to excel from other option of electrolytes.

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