A Special Sulfur Based Polymer as a Processing Material for Electrodes

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Abstract: sustainable development is the demand of current energetic era and generation of cheaper and best quality of electrode materials is the one of them. Elemental sulfur has a great potential for it. The electrochemical properties of sulfur are not studied too widely. Here we are going to develop a material for electrode, which can be used in various kinds of rechargeable batteries. The method adopted for this purpose is “Inverse Vulcanization”.

The polymeric material that is synthesized have very good electrical and thermal properties, those are absent or are up to a very low level in elemental sulfur. Many attempts are made to for generation of such a novel material and it is one of them. Styrene is one the compound that is used here to stabilize the radical terminals of sulfur and makes it a processable material.

Introduction

Simply, the insertion of sulfur atoms in between the two different polymeric chains of natural rubber to make it processable material, is known as vulcanization. But taking sulfur in its elemental state and making its polymer via free radical chain opening route, this is known Inverse Vulcanization. The material generated is novel for electrodes, mainly as cathode. This method has been used and developed four to five decades. Many people has tried to make a cheaper and processable material by taking maximum amount of sulfur.

Sulfur is non metal and does not have any kind of electrical properties in its elemental state. A bout 60 million tons of sulfur is generated annually by Hydrodesulphurization (HDS) process in petroleum industries, but have a very limited uses. So everyone is looking for the utilization of this waste product of our industries for the good healthy and good environment.

We are going to synthesize a material which has maximum content of sulfur and good electrical specific capacity with lowest relative price. Many sulfur based polymers and nano composites has been generated but this polymer is one the best polymer out of them and easy to prepare. Lithium batteries have high energy density and are rechargeable in nature. But the cathodic material used in them is lithium cobalt oxide (LiCoO2), which is toxic and have high relative cost.

The shown below give relative information about various kind of cathodic materials used in batteries

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Capacity(mAhg^-1)</th>
<th>Voltage (V)</th>
<th>Relative Price</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO2</td>
<td>275</td>
<td>3.7</td>
<td>1</td>
</tr>
<tr>
<td>LiMn2O4</td>
<td>148</td>
<td>3.8</td>
<td>0.17</td>
</tr>
<tr>
<td>Poly(S-styrene)</td>
<td>1672</td>
<td>2.1</td>
<td>0.017</td>
</tr>
</tbody>
</table>

The table clearly shows the potential of sulfur for cathodic material. Polymeric sulfur with DIP (to stabilize the diredical ends of sulfur) has been reported but are going to increase the electrical and thermal properties of polymer by using Styrene as a replacement of DIP.

Sulfur in its elemental state (S8) has the melting point in the range of 120C to 124C due to the presence of its different crystalline forms. The melt sulfur has a yellow colour which changes when the ring opening will occurs. This opened chain has 30 to 32 sulfur elements. All this will occurs at a temperature about 140 C to 150C. But this form of sulfur is highly unstable due to the presence of radical ends.

Sulfur melts form at 140 c&Atthis stage of maximum polymerization the target is to stabilize the diredical ends of polymeric sulfur. This can be done by using Styrene.

Experimental

10 mmol of elemental sulfur was taken in glass beaker that is already fitted with magnetic stir; this was heated to a temperature of 140 C. A clear
solution having orange colour will form that shows the occurrence of ring opening polymerization (ROP). 2m moles of styrene was added at this stage (if temperature exceeds to 140 C then styrene may evaporate). Heating of five to ten minutes will give a clear viscous solution of poly(s-styrene). Sample was taken from it and fitted into moulds to get micropatterned poly(s-styrene).

Result AND Discussion

The unresolved 1H NMR spectra of pure styrene shows five peaks out of these three are corresponding to the vinyl hydrogen, those behave as distreoismers.

But the 1H NMR of the polymer shows the shielding of the protons which shows the addition of the sulfur atoms across the vinyl carbon. The shift is from 5.18 ppm to 3.27 ppm, this shows the conversation of the vinyl group to the single bonded carbon group. The same thing can be confirmed from the 13 C NMR spectra of pure styrene and the polymer having the styrene. The shift is from 113 ppm to 41.0 ppm for the vinyl carbon.

1H NMR of polymer

MASS spectra

LD- MS of the poly(S-styrene) gives very important information about the presence of the -S-S- bond. The low molecular weight unit have high crystallization character and gives the regular mass spectra with peaks at the separation of 32 m/z unit. This peak shows the –S-S- bond presence.

Electrochemical properties

The electrochemical batteries consist of poly(S-styrene) as an active material were fabricated and evaluated by cyclic voltametry and also by battery cycling experiments. This CV experiment confirms that the properties of this polymer and sulfur are very close. Battery shows a discharge capacity of 1100 mA/g.
Conclusion

Overall experiment confirms that this is one of greenest step towards the preparation of a cheaper cathodic material for rechargeable batteries. The battery with cathode of poly(S-styrene) high capacity of retention and long term cyclic strength. This experiment is next step towards the synthetic uses of industrial waste, sulfur.

References