A cross-linking poly(urethane acrylate) binder for Si negative electrode in Li-ion batteries (LIBs)

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Abstract : For the fabrication of the Si negative electrode in Li-ion batteries (LIBs) containing the cross-linking polymer binder, in this work, the urethane acrylate (UA) oligomer was synthesized via a simple synthetic process. The cross-linked poly(urethane acrylate) (CPUA)/carbone black (CB)/Si composite (CPUA/CB/Si composite) was fabricated through reactions between their reactive vinyl segments in the UA oligomer. Interestingly, the CPUA/CB/Si composite showed better cycle performance than the poly(vinylidene fluoride) (PVdF)/CB/Si composite (PVdF/CB/Si composite) and the polyurethane (PU)/CB/Si composite (PU/CB/Si composite). The CPUA/CB/Si composite had the best lithiation of about 2586 mAh g^{-1}. The UA oligomer showed a good compatibility with the electrode materials and current collector after and before a curing process.

Keywords : cross-linking binder, Si, PVDF, oligomer, composite.

1. Introduction

The Si negative electrode in LIBs has been attracting much attention since Si as an anode active material offers the highest theoretical specific capacity (3572 mAh g^{-1}) [1-3]. Nevertheless, the disadvantage of Si negative electrode in LIBs is a large volume change of Si during cycling [4-6l. Therefore, a few researchers have studied on binders such as poly(vinylidene fluoride) (PVdF) [7], carboxymethyl cellulose (CMC) [8], styrene butadiene rubber (SBR) [9] and acrylate polymer [10] since the robust structure of

polymeric binder to the LIBs anodes is a promising means to guarantee a high capacity electrode. However, these studies focused only on the modification of a linear polymer or a copolymer dissolved in a solvent. Judging from this, since the cross-linking polymer has a very good scratch, chemical resistance, resilient and adhesion [11-13], it can be a good alternative as a binder for Si negative electrode in LIBs. Actually, the cross-linking polymers are insoluble in the general organic solvents due to their cross-linking points. For such a reason, the practical application of them is virtually impossible.

To overcome this drawback, our laboratory has synthesized an UA oligomer containing a 2-hydroxyethyl methacrylate (2-HEMA)-

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based reactive vinyl segment in the backbone. The CPUA/CB/Si composite containing the cross-linking polymer binder was fabricated through a curing process of the UA/CB/Si mixture in a solvent. The purpose of this work was to present a new fabrication process of the Si negative electrode in LIBs containing the cross-linking polymer binder.

2. Experimental

2.1. Materials

In the synthesis of UA oligomer, polypropylene glycol (PPG) (M_w = 1000, Aldrich), polyethylene glycol (PEG) (M_w=1,000, Aldrich), 2,4-toluene diisocyanate (TDI) (Aldrich), 2-HEMA (Aldrich), dimethylacetamide (DMAc, Aldrich), 2,2-azobisisobutyronitrile (AIBN, Aldrich) and N-methyl-2-pyrrolidone (NMP) were used as received. PVdF (KF1100) and Si (d_{avg} = 10 um) were purchased from Kureha Co. and Aldrich and used as received. CB (Denka black) was purchased from Denka Co. used as received.

2.2. Synthesis of the UA oligomer

The UA oligomer was synthesized in a 500 ml 4-neck glass reactor with stirrer, thermometer, reflux condenser and inlet system for nitrogen gas. First, TDI was poured into the reactor at nitrogen state. In order that the isocyanate (-N=C=O) segment of TDI react with the hydroxyl (-OH) segment, PPG was dropped into the reactor at 50℃. Second, in order to introduce the reactive vinyl groups, 2-HEMA was added into the reactor at 60℃ for 3 h. Lastly, PEG was poured into the reactor to react with the residual isocyanate segment at 75℃ for 3 h. The reaction end point was determined by the disappearance of 2270 cm^{-1} corresponding to NCO stretching. The molar ratio of PPG/PEG/TDI/2-HEMA was 1.0/1.0/2.0/1.0. The PU was synthesized except for the

2-HEMA. The molar ratio of PPG/PEG/TDI was 0.5/0.5/1.0. Fig. 1 shows a structure and a cross-linking route of the UA oligomer.
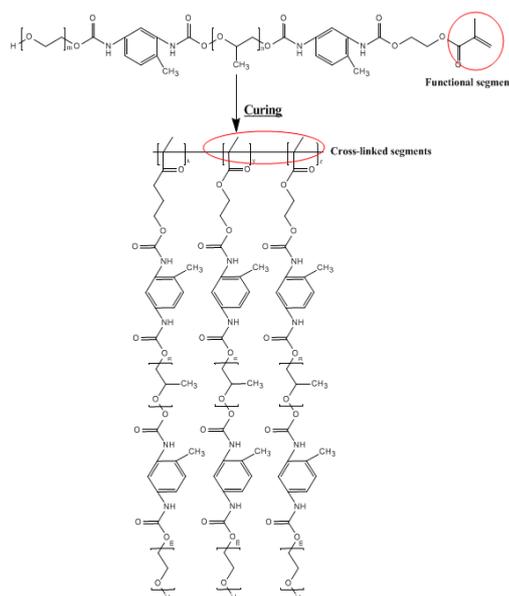

Fig. 1. Structure and cross-linking route of the UA oligomer.

2.3. Fabrication of the CPUA/CB/Si composite

The UA/CB/Si mixture was prepared by direct mixing of 60% Si, 25% CB, 15% UA oligomer and a radical initiator (AIBN) in NMP. The prepared composite mixture was cast on a Cu-foil, and then was cured into a silicone-packed mold to carry out the cross-linking polymerization at 85℃ for 2 h. In order to enhance the inter-particle contacts, the electrode was roll-pressed and dried in vacuum oven at 120℃ for 12 h [7-10]. Whole process for fabrication of the CPUA/CB/Si composite is shown in Fig. 2. Preparation recipes of each CB/Si composite electrode are summarized in Table1.
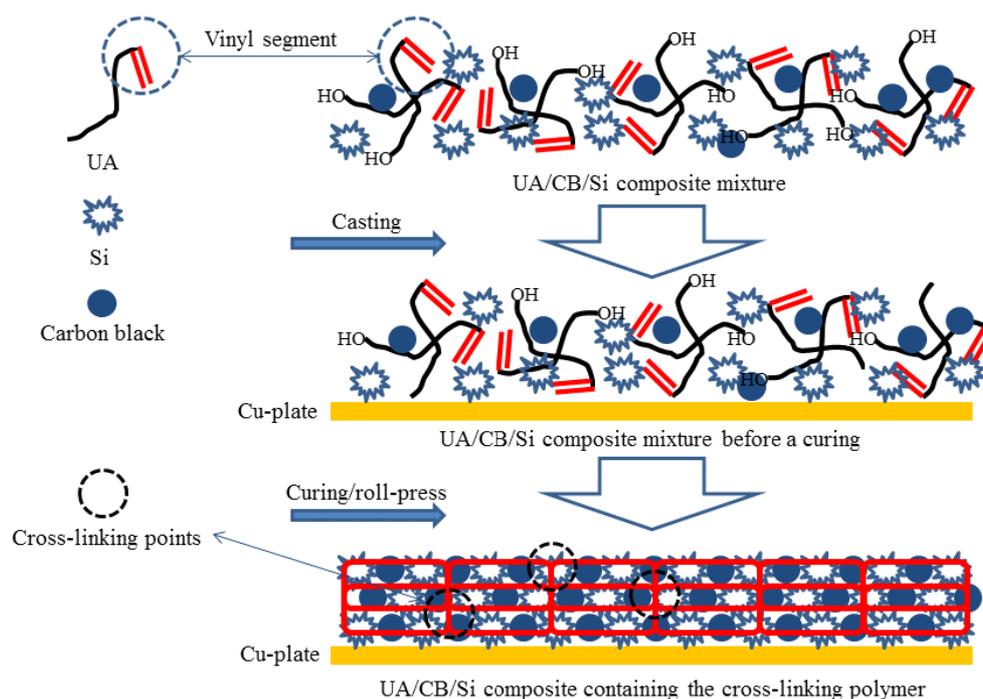
Fig. 2. Schematic illustration for fabrication of the CPUA/CB/Si composite.

Table 1. Recipe of the CB/Si composite electrodes

Sample	Si	CB	PU	PVdF	UA	NMP	AIBN
PVdF/CB/Si composite	0.60 g	0.25 g	–	0.15 g	–	3.0 g	–
PU/CB/Si composite	0.60 g	0.25 g	0.15 g	–	–	3.0 g	–
CPUA/CB/Si composite	0.60 g	0.25 g	–	–	0.15 g	3.0 g	0.005 g

2.4. Measurement

Coin half cells (CR2032) of the electrodes were manufactured in a dry glove box with ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (3:7 vol. ratio) electrolyte containing 1.0 M LiPF$_6$ and the Celgard® commercial trilayer PP/PE/PP separators. The Lithium metal was used as a counter electrode. The galvanostatic cycle of the prepared CB/Si composite was carried out at the voltage range 0~2.0 V with current density of 100 mA/g (WBCS3000 cycler, Wonatech Co.).

On the other hand, the electrolyte uptake (EU) was determined by measuring the change of weight between the wet and dry binder. Binders (size: 0.5 0.5 cm) were soaked in the EC/EMC (3 : 7 vol. ratio) electrolyte solution containing the 1.0 M LiPF$_6$ at room temperature for 48 h. The external binder was wiped off and weighed. The electrolyte uptake of binders was obtained by the following equation:

where W_{dry} and W_{wet} are the weight of the dry and the corresponding electrolyte-sorbed binders, respectively. The electrolyte uptake of the binders was calculated from the average value of W for five binder samples.

3. Results and Discussion

Generally, the electrolyte uptake of binders is one of the important factors that affect the electrochemical properties for Si negative electrode in LIBs because the Li-ions are migrated through the electrolyte-sorbed binder matrix. However, the binders with excessive electrolyte uptake can cause undesirable changes such as low dimensional stability, weak adhesion, low mechanical and low chemical property with electrode particles and current collector during cycling [13,14]. Therefore, maintaining the suitable electrolyte uptake is very important. Fig. 3 shows the electrolyte uptakes of PVdF binder, PU and CPUA binder. At the same condition, the PU (about 352%) and CPUA binder (78%) had much higher electrolyte uptake than the PVdF binder (about 18%). This work indicates that the electrolyte uptake of blending binders was decreased with increasing the cross-linking segments in the PU binder matrix.
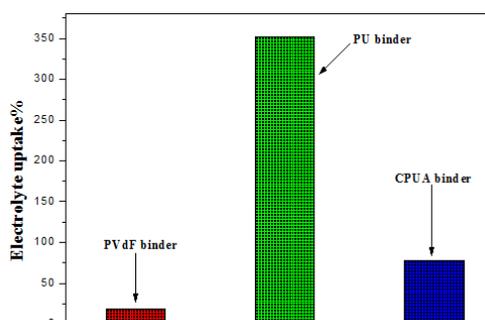

Fig. 3. Electrolyte uptake of the PVdF, PU and CPUA binder.

Fig. 4 (a) shows the lithiationof the CB/Si composite electrodes. At the same condition, the lithiation of them was ranged from about 2316 to 2586 mAh g^{-1}. Out of them, the lithiation of the PVdF/CB/Si composite was about 2359 mAh g^{-1} and was decreased by about 34% compared to the theoretical specific capacity (3572 mAh g^{-1}) of Si. This is possible that the linear-chains of PVdF as a binder increased the Li trap by obstructing the porous surface of Si. As seen in Fig. 4 (b), the delithiation of the PVdF/CB/Si composite was drastically decreased after 1 cycle, and only about 8% (around 202 mAh g^{-1}) of the lithiation was maintained after 15 cycles. Since the electrolyte solution in binders serves as a conducting medium of Li-ions, it is expected that the low electrolyte uptake of PVdF as a binder played a role in decreasing the delithiation of the PVdF/CB/Si composite [15,16]. Meanwhile, the lithiation of the PU/CB/Si composite was similar to that of the PVdF/CB/Si composite. The PU/CB/Si composite showed the worst delithiation. This is considered that the excessive electrolyte uptake of the PU as a binder played a role in decreasing a binding strength in the binder matrix during cycling.

On the other hand, the lithiation of the CPUA/CB/Si composite was about 2586 mAh g^{-1} and was decreased by about 27% compared to the theoretical specific capacity of Si. Interestingly, the lithiation of the CPUA/CB/Si composite was improved compared to the PVdF/CB/Si composite. The CPUA/CB/Si composite showed the best lithiation. This is probably since the Li trap of the binder was alleviated with increasing the electrolyte uptake in the CPUA binder matrix, Moreover, the delithiation of the CPUA/CB/Si composite was maintained by about 13% (around 341 mAh g^{-1}) for 15 cycles and was improved compared to the PVdF/CB/Si composite and PU/CB/Si composite. This is attributed to the fact that the cross-linked networks of the CPUA as a

binder played a role in increasing a binding strength and a role in releasing a volume change of Si during cycling [17,18].
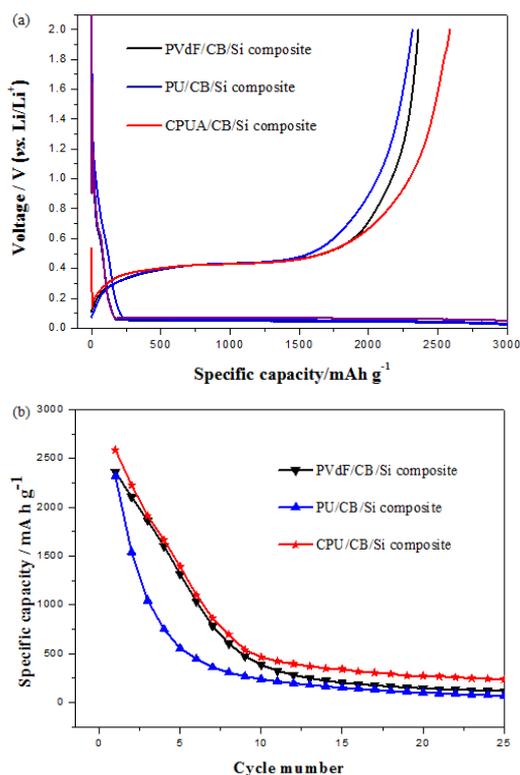

Fig. 4. Lithiation (a) and delithiation (b) of the CB/Si composite electrodes.

4. Conclusions

In conclusion, the CPUA was used as a cross-linking polymer binder to fabricate the Si negative electrode in LIBs. The CPUA/CB/Si composite containing the cross-linked binder system showed better lithiation and delithiation than that of the CB/Si composites containing the linear polymeric-binder system. The CPUA binder had a very high electrolyte uptake in spite of a cross-linked polymer. Further work was to apply the various functional monomers to the Si negative electrode in LIBs through a curing process.

References

1. H.C. Tao, M. Huang, L.Z. Fan, X. Qu, Electrochim. Acta 89 (2013) 394-399.
2. S. Komaba, K. Okushi, T. Ozeki, H. Yui, Y. Katayama, T. Miura, T. Saito, H. Groult, Electrochem. Solid State Lett. 12 (2009) 107-110.
3. J. Bae, S.H. Cha, J. Park, Macromol. Res. 21 (2013) 826-831.
4. J.S. Thorne, J.R. Dahn, M.N. Obrovac, R.A. Dunlap, J. Power Sources 216 (2012) 139-144.
5. P.P. Ferguson, A.D. W. Todd, J.R. Dahn, Electrochem. Commun. 12 (2010) 1041-1044.
6. Q. Yuan, F. Zhao, Y. Zhao, Z. Liang, D. Yan, Electrochim. Acta 115 (2014) 16-21.
7. H. Usui, M. Shimizu, H. Sakaguchi, J. Power Sources 235 (2013) 29-35.
8. H. Buqa, M. Holzapfel, F. Krumeich, C. Veit, P. Novak, J. Power Sources 161 (2006) 617-622.
9. N. Ding, J. Xu, Y. Yao, G. Wegner, I. Lieberwirth, C. Chen, J. Power Sources 192 (2009) 644-651.
10. J. Li, D.B. Le, P.P. Ferguson, J.R. Dahn, Electrochim. Acta 55 (2010) 2991-2995.
11. Z. Chen, L. Christensen, J.R. Dahn, Electrochem. Commun. 5 (2003) 919-923.
12. A. Magasinski, B. Zdyrko, I. Kovalenko, B. Hertzberg, R. Burtovyy, C.F. Huebner, T.F. Fuller, I. Luzinov, G. Yushin, Appl. Mater. Interfaces 2 (2010), 3004-3010.
13. H.K. Park, B.S. Kong, E.S. Oh, Electrochem. Commun. 13 (2011) 1051-1053.
14. J. Guo, A. Sun, X. Chen, C. Wang, A. Manivannan, Electrochim. Acta 56 (2011) 3981-3987.
15. A.K. Rai, J. Gim, L.T. Anh, J. Kim, Electrochim. Acta 100 (2013) 63-71.

16. Y.S. Kim, J. Choi, D. Kim, Macromol. Res. 21 (2013) 49-54.

17. F.M. Hassan, Z. Chena, A. Yu, Z. Chen, X. Xiao, Electrochim. Acta 87 (2013) 844-852.

18. H. Xiang, K. Zhang, G. Ji, J.Y. Lee, C. Zou, X. Chen, J. Wu, Carbon 49 (2011) 1787-1796.