

Crosslinked Poly(acrylamide-co-acrylonitrile) as an efficient binder for Silicon/Graphite anodes of Lithium ion batteries

The electrochemical performance of Si anode is strongly affected by polymer binder, e.g synthetic and bio-derived polymers which containing carboxyl groups, such as alginate[1], polyacrylacid (PAA)[2] and carboxymethyl cellulose (CMC)[3], polyacrylate, compared to conventional fluorinated binders. As of today, poly(vinylidene)difluoride (PVdF) is the most common polymer used as a binder due to its electrochemical stability with some extend of adhesion to electrode materials and current electrode. However, PVdF requires the usage of toxic and expensive organic solvent, N-methyl-2-pyrrolidone, during the electrode manufacturing process.[4]

To replace the organic solvent, water soluble binders have already been studied. Nonetheless, the linear chain of these polymer binders is impossible to move down due to the huge volume change of Si during cycling. As a result, polymer chain together with the deformed electrode cannot recover its original state.[1], [2], [5], [6]

In our resent research, we have synthesized highly interactive and conductive binder from the mixture of acrylamide (AM) and acrylonitrile (AN) monomers using ammonium persulphate (APS) and tetramethylethylenediamine (TEMED) as initiators via a free radical copolymerization method as show in the Fig.1a. As our preliminary result, Si/C anode with this new binder is found to have the discharge capacity of 1480 mAh g⁻¹ at 0.5 C and strongly efficient for lithium ion transition compared to that with polyacrylamid (PAM) binder.

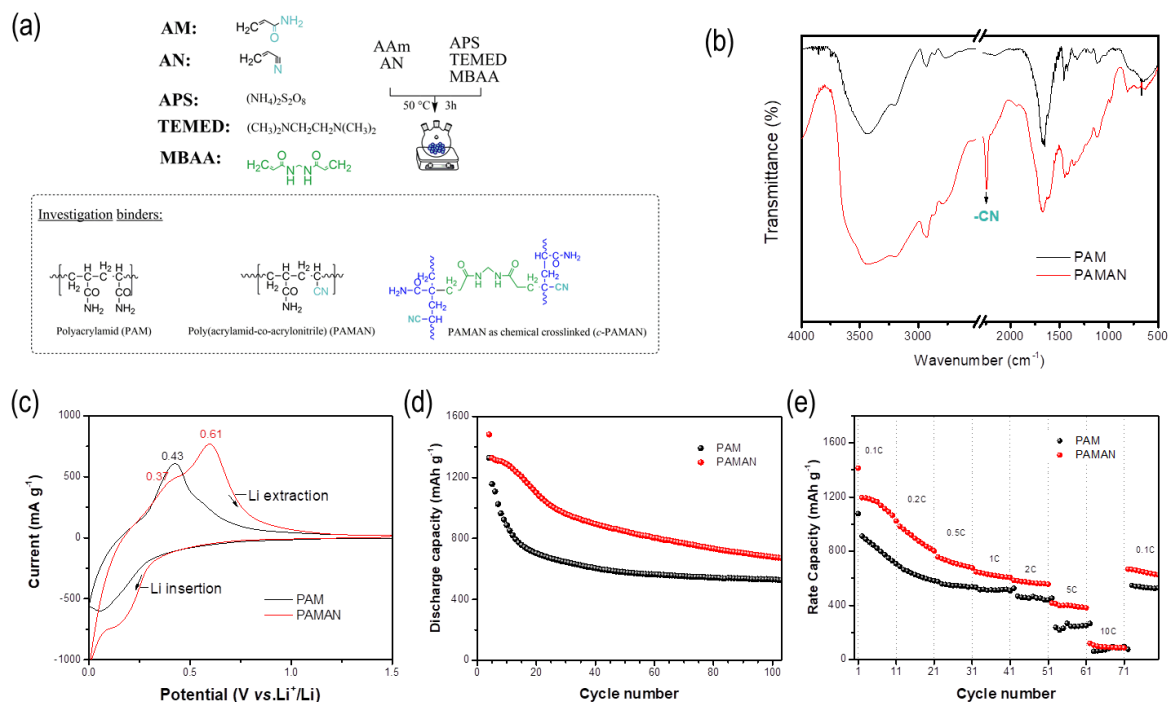


Figure 1: (a) Preparation of PAMAN binders; (b) FTIR spectrum, (c) cyclic voltammogram of Si/C fresh electrode, (d) cycling performance at 0.5C (e) rate performance of Si/C electrode with PAM and PAMAN

The chemical structure of a newly synthetic copolymer binder was observed with the FTIR as shown in Fig.1.b. All main and other characteristic peaks are closely appeared for both synthetic binders such as including PAM and PAMAN spectrum. In the spectra of the PAMAN, the characteristic peak of C≡N at 2241 cm⁻¹ is exhibited[7], [8] and the peak intensity at 2944 increases due to the stretching vibration band of -CH₂ groups compared to PAM. These result confirms the copolymerization of AM and AN monomers.

The electrochemical performance of Si/C electrode containing the binder was employed using galvanostatic cycling at room temperature using CR2032-type coin cell. The cyclic voltammetry (CV, Fig.1c) of Si/C-PAMAN fresh electrode measurement shows two delithiation peaks at 0.37 and 0.61 V and a lithiation peaks at 0.17 V. The anodic and cathodic currents exhibit a narrow and higher in the Si/C-PAM electrode, indicating a polar nitrile group (C≡N) in PAMAN binder chain may be contributed to larger lithium-ion diffusion through Si/C anode, when compared to typical PAM binder. That is in agreement with previous results of Oh et al.[9] The Si/C-PAMAN electrode shows the discharge capacity of 1480 mAh g⁻¹ at current density of 0.5 C as illustrated in Fig.1d. After 100 cycles, the capacity remains 671 mAh g⁻¹ corresponding to 47% capacity retention but it has higher average capacity value of 889 mAh g⁻¹ compared to 628 mAh g⁻¹ for Si/C-PAM electrode. The Si/C-PAMAN electrode achieves 1173mAh g⁻¹ of reversible capacity at 0.1 C (Fig. 1e). Even at high current density of 10 C, the capacity of 122 mAh g⁻¹ is shown and the capacity quickly returns to 647 mAh g⁻¹ when the current is changed back to 0.1 C. Clearly, the Si/C-copolymer binder is favorable to high reversibility.

REFERENCE

- [1] J. Liu *et al.*, "A high-performance alginate hydrogel binder for the Si/C anode of a Li-ion battery," *Chem. Commun.*, vol. 50, no. 48, pp. 6386–6389, May 2014.
- [2] A. Magasinski *et al.*, "Toward Efficient Binders for Li-Ion Battery Si-Based Anodes: Polyacrylic Acid," *ACS Appl. Mater. Interfaces*, vol. 2, no. 11, pp. 3004–3010, Nov. 2010.
- [3] J. Li, R. B. Lewis, and J. R. Dahn, "Sodium Carboxymethyl Cellulose A Potential Binder for Si Negative Electrodes for Li-Ion Batteries," *Electrochem. Solid-State Lett.*, vol. 10, no. 2, pp. A17–A20, Feb. 2007.
- [4] J. Song *et al.*, "Interpenetrated Gel Polymer Binder for High-Performance Silicon Anodes in Lithium-ion Batteries," *Adv. Funct. Mater.*, vol. 24, no. 37, pp. 5904–5910, Oct. 2014.
- [5] B. Lestriez, S. Bahri, I. Sandu, L. Roué, and D. Guyomard, "On the binding mechanism of CMC in Si negative electrodes for Li-ion batteries," *Electrochem. Commun.*, vol. 9, no. 12, pp. 2801–2806, Dec. 2007.
- [6] U. S. Vogl, P. K. Das, A. Z. Weber, M. Winter, R. Kostecki, and S. F. Lux, "Mechanism of Interactions between CMC Binder and Si Single Crystal Facets," *Langmuir*, vol. 30, no. 34, pp. 10299–10307, Sep. 2014.
- [7] H. Mittal, R. Jindal, B. S. Kaith, A. Maity, and S. S. Ray, "Synthesis and flocculation properties of gum ghatti and poly(acrylamide-co-acrylonitrile) based biodegradable hydrogels," *Carbohydr. Polym.*, vol. 114, pp. 321–329, Dec. 2014.
- [8] H. Jia, Z. Huang, Z. Fei, P. J. Dyson, Z. Zheng, and X. Wang, "Unconventional Tough Double-Network Hydrogels with Rapid Mechanical Recovery, Self-Healing, and Self-Gluing Properties," *ACS Appl. Mater. Interfaces*, vol. 8, no. 45, pp. 31339–31347, Nov. 2016.
- [9] L. Gong, M. H. T. Nguyen, and E.-S. Oh, "High polar polyacrylonitrile as a potential binder for negative electrodes in lithium ion batteries," *Electrochem. Commun.*, vol. 29, pp. 45–47, Apr. 2013.