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Title

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Permalink

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Journal

ACS applied materials & interfaces, 6(19)

ISSN

1944-8244

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Publication Date

2014-10-01

DOI

10.1021/am504736y

Peer reviewed

A systematic investigation of polymer binder flexibility on the electrode performance for lithium-ion batteries

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Abstract: The mechanical failure in the electrode interfaces (laminate/current collector and binder/particle interfaces) leads to particle isolation and delamination, which has been regarded as one of the main reasons for the capacity decay and cell failure of lithium-ion batteries (LIBs). Polymer binder provides the key function for a good interface property and to maintain the electrode integrity in LIBs. Triethyleneglycol monomethylether (TEG) moieties were incorporated into polymethacrylic acid (PMAA) with different contents on the molecular level. Microscratch tests of the graphite electrodes based on these binders indicate that the electrode is more flexible with 5% or 10% TEG in the polymer binders. Crack-generation is inhibited by the flexible TEG-containing binder, compared to that of the unmodified PMAA-based electrode, leading to a better cycling performance of the flexible electrode. With 10% TEG moiety in the binder, the graphite half cell reaches a reversible capacity of above 270 mAh/g at 1C rate, compared to a value of ~ 190 mAh/g for the unmodified PMAA binder.

Keywords: polymer binder, flexibility, graphite anode, lithium-ion battery,

1. Introduction

Among all the energy storage devices,^{1,2} rechargeable lithium-ion batteries (LIBs) are widely used as power sources for the portable electronics, and more recently for electrical vehicles and electrical grid storages.³ The wide application of LIBs has boosted the development of novel materials and systems to enhance the energy density and cycle life of LIBs. In a conventional electrode laminate of LIBs, polymer binders are inactive but indispensable components.⁴ Polymer binders, such as polyvinylidene fluoride (PVDF), hold the active materials and conductive additives mechanically in the electrode laminate. Electronically conductive additives, such as acetylene black (AB), are used to enable the electrical conductivity throughout the electrode. The combined polymer binder and conductive additives maintain the mechanical and electronic integrity of the entire electrode. In addition, the polymer binders coat the active material surfaces, so the polymer swells in the electrolyte to provide ionic conductivity.⁵ The mechanical failure in the electrode interfaces (laminate/current collector and binder/particle interfaces) leads to particle isolation and delamination, which has been regarded as one of the main reasons for the capacity decay and cell failure of lithium-ion batteries (LIBs).^{6,7,8} Lee and coworkers introduced a conductive adhesive layer between the current collector and the active material layer, an improved cycling performance was observed for both graphite or graphite/silicon electrodes.⁹ Typically, LIB electrodes rely on polymer binders to attain particle/particle cohesion and electrode laminate/current collector adhesion.¹⁰ An optimized design of polymer binders should be able to eliminate crack generation in the electrode,¹¹ the development of a suitable binder is becoming an important part of the solution to enable the stable cycling of novel electrode active materials, such as high-capacity alloy anodes (Silicon¹² and Tin^{13,14}) and high voltage cathodes.¹⁵⁻¹⁶ The state-of-the-art roll-to-roll lamination process in industry¹⁷ also specifically requires a flexible and ductile nature of the polymer binders and electrode, which helps to avoid crack generation and delamination during processing. Incorporation of triethyleneglycol monomethylether (TEG) moieties in the polymer is supposed to increase both the interface adhesion and the ductility to better eliminate stress-induced fracture.^{18,19} In fact,

polyethyleneoxide (PEO) is known to form stable interface layer between lithium metal and the PEO electrolyte, thus, it is chemically suitable in the anode environment.²⁰

To unveil the role of the polymer binders in the inhibition of failure of electrode interfaces, a rigid polymer binder was chemically modified to gradually improve the flexibility. The different binders were used to fabricate electrode laminates. Micro-scratch tests were conducted to the surface of the electrodes to reveal the different mechanical responses from the electrode made with rigid binder and flexible binder. Graphite electrodes assembled using the modified flexible binder can inhibit the generation of cracks, leading to an improved cell cycling performance.

Figure 1. (a) The synthetic route for the TEG-containing PMAA polymers, with flexible and rigid structures highlighted, respectively. DSC curves of (b) PMAA, (c) PMAA-5%PTEGMA, and (d) PMAA-10%PTEGMA, indicating the glass transition temperatures (T_g) of different polymers.

2. Results and discussion

Synthesis of the PMAA-based polymer binders: We use poly (methacrylic acid) (PMAA) as model polymer binder, which offers high concentration of functional groups (one carboxylic acid group in each repeating unit) and allows facile structural modification via copolymerization.²¹ There are several reasons that PMAA was used as the polymer binder to study the influence of TEG in this study. Polymers such as PMAA and polyacrylic acid (PAA) with high concentration of acid functionality gain wide application as polymer binders for LIBs.^{22,23} However, the negative side of this structure is that PMAA and PAA-based electrode laminates are rigid and brittle, which easily go through delamination during the roll-to-roll electrode handling in industry.²⁴ Also, due to the high concentration of carboxylic acid groups, PAA and PMAA-based electrodes tend to absorb large extent of water and ultimately lead to swelling of cells (gas generation) in the course of use, modification of the PMAA and reducing the amount of acid functional groups are advantageous. Ethylene glycol-based polymers have been intensively investigated as solid-state electrolytes for several decades,²⁵ yet, the use of pure poly(ethylene glycol) (PEG) as polymer binders seems less attractive.²⁶ PEG has a high solubility in carbonate-based electrolytes, this should lead to an uncontrolled swelling of the electrode in the electrolyte, the electrical contact between the active materials and the electrode will be lost.²² However, instead of using pure PEG polymer as binder, our recent result indicates an advantage of incorporating ethylene glycol structure to modify the binder property. A balanced multifunctionality with high electronic conductivity, mechanical adhesion, ductility and electrolyte uptake was realized via modification using ethylene glycol,²⁷ a full-capacity alloy anode was thus obtained based on this new binder. There are several advantages a binder could gain from ethylene glycol structural moiety. Because of the good lithium ion conductivity and the solubility with carbonate-based electrolytes, polymer binders modified by ethylene glycol have a good electrolyte uptake property, which facilitates the lithium ion transport between electrolytes and electrode active materials. As a polymer segment with low glass transition temperature (T_g , at about -60 °C), Ethylene glycol enables a more ductile nature of the polymer binder, Triethylene glycol methacrylate (TEGMA) is chosen as a co-monomer (Figure 1a) to bring ethylene glycol moiety into the polymer binder. The methacrylate structure in this monomer enables a copolymerization chemistry with MAA (Figure 1a), a uniform distribution of

TEGMA in the final polymer binder is achieved. Incorporation of TEG structure into the polymer enables us to systematically investigate the influence of the mechanical properties of the binder when used in LIBs. A typical free radical polymerization is conducted using azobisisobutyronitrile (AIBN) as an initiator and toluene as a solvent. The reaction was performed at 70 °C for ~24 hours before precipitation in hexane to remove residual monomers. Three different copolymers were synthesized in the lab, with 0 wt%, 5 wt%, or 10 wt% TEGMA monomers, the final polymers were labeled as PMAA, PMAA-5%PTEGMA and PMAA-10%PTEGMA. The T_g of the different polymers were characterized using Differential Scanning Calorimeter (DSC), as shown in Figure 1b to c. PMAA has a T_g of ~108 °C, which is consistent with the value in literature. Even with a small amount of PTEGMA component (5%), T_g is lowered to 93 °C (Figure 1c), and this value does not change much (94 °C, Figure 1d) when PTEGMA is increased to 10%. The lowered glass transition temperature indicates a more flexible nature with the incorporation of PTEGMA structure.

Figure 2. ^1H NMR spectra of PMAA-based binders collected in d_6 -DMSO, with asterisks marking the solvent signals arising from the proton residuals due to incomplete deuteration, and the signals corresponding to TEG highlighted.

The structures are confirmed by the ^1H NMR spectra shown in Figure 2. The doublet at 0.9~1.1 ppm is a clear evidence of the polymerized methacrylate polymer, corresponding to the $\text{CH}_3\text{-C}(\text{CH}_2)\text{-}$ substructure. While the singlet at 12.4 ppm represent the carboxylic acid proton in PMAA. The broad

signal between 1.6~2.1 ppm is assigned to the $-\text{CH}_2-\text{C}(\text{CH}_3)-$ substructure in the polymer backbone. The successful incorporation of TEG structure into the synthesized polymer binder is corroborated by the signals between 3.3~3.6 ppm, which corresponds to the $-\text{CH}_2-\text{CH}_2-\text{O}-$ substructure in the TEG side chain.

	M_n	M_w	PDI
PMAA	220,000	440,000	2.0
PMAA-5%PTEGMA	230,000	470,000	2.0
PMAA-10%PTEGMA	210,000	460,000	2.2

Table 1. The molecular weights and PDIs of the synthesized PMAA-based polymer binder.

A high molecular weight is a prerequisite for good mechanical and binding property, which is stringently required for a polymer binder. Gel Permeation Chromatography (GPC) was used to characterize the molecular weight and polydispersity index (PDI) of the PMAA-based polymers with different TEG contents, as shown in Table 1. All the three different polymers have molecular weights above 200,000 Dalton. The relatively large PDI of ~2.0 is typical for a free radical polymerization.

Physical property of the polymers and electrodes: A microscratch test²⁸ was carried out on the pristine electrode samples using the PMAA-based polymers, in order to study the influence of TEG on the mechanical properties of the laminates, shown in Figure 3 a and b. A composite electrode model proposed by Qi and Li's recent work¹⁰ was used to explain the microscratch test results. In the microscratch test, the force applied onto the micro-indenter tip was gradually increasing, thus in a rigid polymer like PMAA, the particles were pushed onto the sides and the tip gradually goes down into the electrode laminate to give a negative scratch depth. For compliant polymers, on the other hand, the particle/particle cohesion was stronger and the particles were difficult to push onto the sides. As the micro-indenter tip started to plow, the particles were accumulated in front of the diamond tip. This tends to lift up the micro-indenter tip. The final scratch depth is ~ 0 for the PMAA-5%PTEGMA, and the diamond tip was even pushed upward for PMAA-10%PTEGMA, giving a positive scratch depth. A lot of polymer binders for LIBs, such as polyacrylic acid (PAA), polymethacrylic acid (PMAA), and carboxymethyl cellulose (CMC),

have high Young's modulus (elastic modulus). Electrode laminates based on these rigid binders tend to generate cracks under a high-stress situation, leading to laminate/current collector delamination and particle/particle isolation, it becomes more serious for the high-capacity alloy anodes.²⁹ TEG structural moiety in the polymer binders enables a more compliant nature, which could better accommodate the volume change of active material, less stress will be accumulated in the binder, as well as at the interface between the binder and the active materials.

Figure 3. (a) Scratch depth and (b) Coefficient of Friction vs. scratch distance in the scratch test of different PMAA-based binders, (c) peel test results, SEM images after scratch tests of (d)(d1) PMAA, (e)(e1) PMAA-5%PTEGMA, and (f)(f1) PMAA-10%PTEGMA binders. The scale bars are 100 μm for (d)(e)(f), 10 μm for (d1)(e1)(f1).

The Coefficient of Friction (COF) in the scratch test reflects the composite nature of the electrode and the mechanical properties of the polymer binder. As shown in Figure 3b, the PMAA laminate shows a similar behavior as PVDF-based graphite laminate, the COF increases rapidly with increasing normal

load because the micro-indenter tip plowed and slid on the electrode surface. Further increase of the normal load enabled a steady state of the COF. TEG-containing polymer binders, on the other hand, exhibited a higher COF from the initial stage of the test, this is consistent with their more compliant and higher binding strength, which leads to stronger interaction with the polar diamond tip used in the tests. The morphologies of the electrode after scratch test indicate obvious difference, as shown in Figure 3 d, e, and f. Rigid polymer like PMAA was pushed away to the sides by the tip during scratch test, a clear scratch track is shown. With more TEG content in the polymer, the binder becomes more ductile and the scratch track becomes less obvious. In the case of the PMAA-10%PTEGMA-based laminate, it is even difficult to see the scratch track under SEM. A scratch test simulates the stress induced by the volume change of electrode active material, this result essentially indicates that more flexible binders such as PMAA-5%PTEGMA and PMAA-10%PTEGMA provide higher tolerance of the volume change through its optimized ductility.^{30,31} Note that this property is especially important for the recent development of high-capacity alloy anodes for LIBs.³²

The improvement on the flexibility of the polymer was also corroborated by the adhesion tests in Figure 3c.³³ As shown in the microscratch test, a brittle polymer binder like PMAA provides low particle/particle cohesion strength, which results in a weak load transfer capability. This explains the peel-test behavior of PMAA laminate. A small peel-off work load (~ 2 N) was shown initially, as the testing proceeds this value fluctuated until an electrode failure. As more compliant polymer binder is supposed to significantly strengthen the mechanical binding force and enhance the particle/particle cohesion strength, the peel-off work load started with a high value (~ 5 N for PMAA-5%PTEGMA and ~ 7 N for PMAA-10%PTEGMA), confirming this high cohesion strength. Introduction of TEG structural moiety successfully enhanced the adhesion force, and this enhancement was more obvious with more TEG content in the binder.

Electrochemical performance

Figure 4. Cyclic voltammetry (CV) of (a) PMAA, (b) PMAA-5%PTEGMA, and (c) PMAA-10%PTEGMA, with the solvent decomposition signals highlighted.

To assess the electrochemical stability of the polymer, CV of the different binders was performed, as shown in Figure 4. The working electrode was a copper foil coated with polymer film without graphite, using lithium foil as counter and reference electrode with EC/DEC, 1M LiPF₆ as electrolytes.⁴ Electrolyte decomposition occurs with both polymers in the first cathodic scan, but no additional current flowed in the voltammogram in the following cycles. All the three synthesized polymer binders are electrochemically stable as polymer binders for the negative electrode, considering that lithium intercalation into graphite occurs below 0.2V vs. Li/Li⁺.

Figure 5. (a) The electrolyte uptake of the polymer binders after 48 hours in EC/DEC=1, 1M LiPF₆, (b) the cell impedance based on different binders. Impedance was taken after 1 cycle at C/25, and rest for 4 hours after half lithiation in the second cycle.

The scratch test shown in Figure 3 only indicates the mechanical property of the binder and electrode at a dry state. Polymer binders in an electrode laminate need to be swelled by lithium ion electrolytes to be ionic conductive, the electrolyte uptake test was done using self-standing polymer samples immersed in the electrolytes. The absolute value of electrolyte uptake is highly affected by the dimension of the testing sample. The polymer bulk sample is a disk with an area of 3.8 cm² and a thickness of around 1 mm. The weight increase after 48 hours is shown in Figure 5a, which shows that PMAA has the highest swelling degree due to the high polarity of the carboxylic acid groups in the polymer backbone. The swelling becomes smaller with incorporation of the PTEGMA structure, which directly influences the cell impedance shown in Figure 5b. PMAA, with the highest electrolyte uptake, enables a better ionic conductivity and smaller impedance; incorporation of PTEGMA leads to smaller swelling degree and higher cell impedance. Although we focus on the influence of binder flexibility, but the modification of the polymer structure inevitably changes other relevant properties.

Figure 6. (a) Cycling performance of graphite half cells with different binders, C/25 for 2 cycles, C/10 for 5 cycles and then 1C, (b) the 1st cycle voltage curves, (c) the voltage curves of electrode with PMAA binder and (d) the voltage curves of electrode with PMAA-10%PTEGMA binder.

The cycling performance of the different PMAA-based binders are shown in Figure 6a, all the cells were put into formation procedure by C/25 for 2 cycles, C/10 for 5 cycles before the long-term 1C cycling. PMAA is able to enable a stable cycling performance of the graphite electrode, which was also shown by others.²¹ To further improve the cell performance, the TEG structural moiety in the binder shows advantage in the slow cycling, both 5% and 10% TEG enable a relative higher specific capacity compared to unmodified PMAA binder. The cell gains a reversible capacity of ~320 mAh/g in the formation cycles for PMAA, while with TEG contents this value is enhanced to ~335 mAh/g. When the cycling rate was increased to 1C, 5% TEG content seems not enough to enhance the cell performance, both PMAA and PMAA-5%PTEGMA show similar performance, with a reversible capacity of ~190 mAh/g at 1C rate. The PMAA-10%PTEGMA, on the other hand, enables a stable cycling at 270 mAh/g at 1C.

The first cycle voltage curves are shown in Figure 6b, compared to PMAA, incorporation of PTEGMA helps to gain more capacity out of the graphite anode. The higher capacity and improved rate capability by PTEGMA-containing polymer binder are further corroborated in Figure 6c and d. About 10% capacity loss is shown from C/25 to C/10 for the PMAA-based cell, although the capacity values are almost the same for PMAA-10%PTEGMA at C/25 and C/10 rates. Note that PMAA-10%PTEGMA shows the largest interfacial impedance data in Figure 5b, but this binder enables a well-improved cell cycling performance, which further confirms the advantage of a flexible binder.

Figure 7. SEM images of graphite electrodes using (a) PMAA before cycling, (a1) PMAA after 1 cycle, (b) PMAA-5%PTEGMA before cycling, (b1) PMAA-5%PTEGMA after 1 cycle, (c) PMAA-10%PTEGMA before cycling, and (c1) PMAA-10%PTEGMA after 1 cycle at C/25. The scale bars are 10 μm .

The microscopic morphologies of the pristine electrodes assembled using the three different binders are shown in Figure 7 a, b, and c.^{34,35} All the SEM images show similar micro-structures, an appropriate porosity is shown for all the PMAA-based binders with a porosity of $\sim 50\%$. The graphite particles are uniformly distributed. There is no aggregation of polymer binder. The polymer coating is uniformly coated on the surface of graphite particle in all cases because of the strong interaction between the carboxylic groups and graphite surface.^{4,36} The swelling of the polymer coating by electrolytes enables a good lithium ion transport between graphite and electrolytes. Figure 7 a1, b1, and c1 show the electrode morphologies after the initial charge-discharge cycle at C/25. A good solid electrolyte interphase must have been formed since a good cycling performance was obtained (Figure 6) with all the three different binders, although the SEI is not visible in the SEM images.^{37,38} These images indicate a thin SEI, which implies that the PMAA-based binders suppress the electrolyte decomposition²¹ and this is beneficial for a good electrochemical performance.

		PMAA	PMAA-5% PTEGMA	PMAA-10% PTEGMA
1 st cycle (C/25)	Q_c^a (mAh/g)	316.3	330.8	326.4
	η^b (%)	92.09	85.06	88.97
7 th cycle (C/10)	Q_c^a (mAh/g)	315.1	330.12	325.7
	η^b (%)	99.61	99.23	99.49
100 th cycle (1C)	Q_c^a (mAh/g)	194.9	196.0	272.9
	η^b (%)	99.97	99.96	99.96

^a charge (delithiation) capacity ^b coulombic efficiency

Table 2. Electrochemical data of the graphite half cells with different PMAA-based binders.

The major electrochemical data of the graphite half cells from the different PMAA-based binders are shown in Table 2. Although the incorporation of TEG in the polymer binder induces smaller 1st cycle coulombic efficiency (85.06% for PMAA-5%PTEGMA and 88.97% for PMAA-10%PTEGMA) compared to the unmodified PMAA binder (92.09%), the reversible capacity of TEG-based electrodes are higher. TEG enables a better wetting of the electrode laminate, which may induce more SEI formation and lower CE. At 100th cycle and 1C rate, PMAA-10%PTEGMA enables a reversible capacity of 272.9 mAh/g with a 99.96% CE. PMAA and PMAA-5%PTEGMA, on the other hand, show capacities at ~195 mAh/g.

Figure 8. (a) Schematic of rigid binder-based electrodes in the process of Li^+ insertion and extraction, (a1) SEM image of the rigid binder-based graphite electrode after cycling, showing electrode cracking, (b) schematic of flexible binder-based electrodes in the process of Li^+ insertion and extraction, and (b1) SEM image of the flexible binder-based graphite electrode after cycling.

The enhanced cell performance based on the flexible TEG-containing polymer is explained in Figure 8. Lithiation of the graphite causes $\sim 10\%$ volume expansion, polymer binder/AB materials sitting next to these graphite active particles were pushed away in the final lithiated stage; these graphite particles shrink back to the original volume during delithiation process, which induces stress in the electrode laminate. Although the high density of the carboxylic acid functional groups in PMAA facilitates the interfacial interaction between graphite particle surface and the polymer, they make PMAA a very rigid and brittle structure. It is not able to tolerate the stress during excessive cell cycling and the electrode generates cracks (Figure 8a1), which leads to graphite particle isolation and disintegration of the laminate in the local sites. This explains the reduced electrochemical performance shown in Figure 6.³⁹ As a well-known flexible structural moiety, the TEG-containing PMAA improves the flexibility of the polymer and avoids

crack-formation during the handling of electrode laminate and cell cycling (Figure 8b and b1), resulting in an improved cell performance.

3. Conclusions

In conclusion, this study demonstrates the systematically varied mechanical properties of an electrode binder and the impact on the electrochemical performance of the electrode. A brittle PMAA was used as a model compound, and TEG component was introduced toward formation of soft binders to improve the battery performance of graphite anode in LIBs. The micro-scratch test demonstrated the different mechanical responses of the electrodes made with different PMAA-based binders. The electrode made with softer binder can better tolerate stress exerted by micro-scratch. This mechanical response test correlates well with the electrochemical test of the electrode. The electrochemical performance shows that with 10 wt% TEG content, an enhanced cell cycling performance with a reversible capacity of ~270 mAh/g at 1C was achieved, compared to the value of 190 mAh/g for the unmodified PMAA polymer binder. The origin of the improvement is from the improved flexibility of the binder and electrodes, which help inhibit laminate/current collector delamination and particle/particle isolation during lithiation and delithiation of the graphite. This work sheds light on the design of polymer binders in lithium ion batteries, especially for the high-capacity alloy anodes such as silicon and tin.

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ACKNOWLEDGEMENT

This work is funded by the Assistant Secretary for Energy Efficiency, Vehicle Technologies Office of the U.S. Department of Energy, under the Batteries for Advanced Transportation Technologies (BATT)

Program. NMR measurements were performed at the Molecular Foundry. Electron microscopy experiments were conducted at the National Center for Electron Microscopy (NCEM). The two facilities are located at Lawrence Berkeley National Laboratory (LBNL), and are supported by the Director, Office of Science, Office of Basic Energy Sciences, of the US Department of Energy under contract no. DE-AC02-05CH11231. Neslihan Yuca thanks the funding opportunity provided by The Scientific and Technological Research Council of Turkey (TUBITAK) in Ankara, Turkey.

SUPPORTING INFORMATION

Details of the materials characterization, FTIR of the synthesized binders, and rate performance of the cells. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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