



Effect of high adhesive polyvinyl alcohol binder on the anodes of lithium ion batteries

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ABSTRACT

High molecular weight (MW) polyvinyl alcohol (PVA) was synthesized by two-step polymerizations and employed as an anodic binder of lithium ion batteries (LIBs). Numerous hydroxyl groups in PVA formed strong hydrogen bonds with both active materials and the current collector. These strong hydrogen bonds led to an increase in the amount of binder covering the surface of active materials and significantly enhanced the adhesion strength of electrodes. The high MW PVA binder showed much better cyclic performance for silicon/carbon anodes than polyvinylidene fluoride (PVDF) and polyacrylic acid (PAA) binders.

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1. Introduction

Over the past 20 years, four main materials of LIBs, cathodic and anodic active materials, separators, and electrolytes have been extensively studied and tremendous progress has been achieved in their fields. On the other hand, much less attention has been given to the polymer binder holding active materials together with the current collector. In recent years, a few studies on the binder have been motivated by the potential to significantly enhance the performance of high capacity anodes [1–5].

With the modification in high capacity materials, a novel binder could be one possibility to resolve the abrupt drop in cyclic capacity occurring on high capacity electrodes. So far, there have been a few studies on the modification of existing PVDF or carboxymethyl cellulose(CMC) binder systems for high capacity anodes. Using an elastomeric fluorine polymer such as poly(vinylidene fluoride–tetrafluoroethylene–propylene), Chen et al. [6] improved the capacity retention of $\text{Si}_{0.64}\text{Sn}_{0.36}$. In the case of water soluble binder systems, most of modifications have been focused on either changing the amount of metal salts in CMC and the ratio of styrene-butadiene rubber to CMC or applying other types of celluloses and emulsified binders [1,7–10].

More recently, acrylate polymers have been studied as a binder [2,3,11]. Magasinski et al. [3] showed that polyacrylic acid(PAA) containing carboxyl groups maintained excellent cyclic retention of carbon-coated silicon nanopowders due to hydrogen bonding with active materials. In this sense, PVA containing numerous hydroxyl

groups could be a very good choice as a binder for high capacity anodes since the hydroxyl groups can form very strong hydrogen bonds with both active materials and the current collector. In this work, high MW PVAs, which are not commercially available, were manufactured and applied as binders for both graphite and silicon-graphite materials. Important preliminary tests were performed to investigate the effects of PVA binder on electrochemical characteristics and these were compared with other binder systems.

2. Experimental

High MW PVAs were synthesized by the hydrolysis of polyvinyl acetate(PVAc) polymerized using vinyl acetate monomers at different reaction temperatures from 35 °C to 50 °C:



For convenience, in what follows, the PVA polymerized at 35, 40, 45, and 50 °C will be designated PVA35, PVA40, PVA45, and PVA50, respectively. More detailed procedures for PVA polymerization are described in the open literature [12]. Through gel permeation chromatography (GPC) and nuclear magnetic resonance(NMR) analyses, the degree of polymerization (DP) of PVAc, i.e., the value of n in eq. (1), and the degree of saponification (DS) of PVA were determined. Here DS indicates the number of hydroxyl groups (–OH) in 100 vinyl units of PVA. For instance, 90% DS means that 90 hydroxyl groups exist in 100 vinyl units while the remaining 10 are acetate groups (–OCOCH₃).

Using the synthesized PVA binders, both graphite and silicon/graphite electrodes were manufactured and compared with the electrodes employing commercially available PVDF or PAA binders.

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These were purchased at Sigma-Aldrich. The MWs of PVDF-L, PVDF-H, PAA-L, and PAA-H in Table 1 were 180,000, 530,000, 450,000, and 3,000,000, respectively. The electrodes were composed of graphite or Si/graphite (85 wt.%), vapor grown carbon fiber (5 wt.%), and 10 wt.% binder. Nanosized-silicon (KCC Co., Korea, $d_{\text{avg}} = 20\text{--}30\text{ nm}$) particles were mechanically mixed with commercial graphite (Sodiff Co., Korea, $d_{\text{avg}} = 10\text{--}20\text{ }\mu\text{m}$) in a planetary ball-mill (Pulverisette 7, Fritsch) for 2 h and the weight ratio of silicon to graphite was 0.42. To measure the adhesion strength of an electrode [11], 180° peel tests of electrode strips (10 mm width) were performed using a texture analyzer (TA-PLUS, Lloyd Instruments Ltd.). The surface coverage of electrodes was measured by X-ray photoelectron spectroscopy (K-alpha, Thermo Fisher) using an Al K α X-ray source scanning from 0 to 1350 eV.

The CR2016 coin half-cells of the electrodes were assembled in an argon-filled glove box with 1 M LiPF₆ (Panaxetec Co., Korea) dissolved in a 1:1:1 (v/v/v) mixture of EC/DMC/EMC. The cells were galvanostatically discharged to 0.005 V and charged to 1.0 V at a C/2 rate using a cycler (WBCS3000, WonAtech Co.). Electrochemical impedance spectroscopy (EIS) and cyclic voltammograms were also performed a frequency range of 0.01 Hz to 100 kHz and at a scan rate of 0.5 mV/s, respectively.

3. Results and discussion

The adhesion strength between active materials and current collector is a critical issue for high capacity active materials, experiencing significant volume change during the charge/discharge processes. As shown in Table 1, both C and Si/C electrodes containing PVA binders showed much higher adhesion strength than those containing PVDF binders. These are due to the strong hydrogen bonding of hydroxyl groups in PVAs. Using NMR analysis, all of the four PVA samples showed DS higher than 90%, indicating that most of the functional groups in PVA are hydroxyl groups. These hydroxyl groups form tight hydrogen bonds with the functional groups on active materials and the current collector, whereas the fluorine atoms in PVDF form weak hydrogen bonds with them [13]. Alternatively, as seen in Table 1, an increase in DP (or MW) of PVAc, the precursor of PVA, enhanced the adhesion strength. High MW polymers form more flocculated structures with active materials by longer polymer chains and thus increase the adhesion strength [13].

The strong hydrogen bonding also gave rise to a good distribution of binder on the surface of active materials by increasing the interaction between binder and active materials. Using XPS, the surface atomic fractions of both polymeric binders and electrodes were measured and are listed in Table 2. As expected, the PVDF binder showed that the atomic ratio of fluorine to carbon was approximately 1. Since the surface atomic fraction of fluorine on the PVDF-containing electrode is about 13%, 26% of the total surface may be covered by the PVDF binder. On the other hand, the surface oxygen composition due to PVA is about 14% and thus the PVA binder covers approximately 49% of the total surface, which is much higher than the PVDF binder. This also contributes to the extremely high adhesion strength of PVA binders.

Table 2

Surface atomic percentages of PVDF- and PVA-containing electrodes.

Sample	C	F	O	Impurities
PVDF-L	50.9	48.5	0.6	
PVDF-L electrode	85.6(13.3)*	(12.7)*	1.7(0.2)*	
PVA45	69.4		28.4	2.2
PVA45 electrode	82.1(35.0)*		15.9(14.3)*	2.0

* The calculated values in parentheses indicate atomic fraction (%) due to binder.

A thin binder film was immersed in a 1:1:1 EC:DEC:EMC solution at room temperature for 48 hours and we measured the swelling ratio, i.e., the weight ratio of the amount of electrolyte uptake to the binder film before swelling. This result is also listed in Table 1. High MW PVAs absorbed smaller amounts of electrolyte than low MW PVAs and PVDF films. Generally, the electrolyte uptake of binder can weaken its binding strength, even though it is necessary for the migration of lithium ions through the binder. In a high capacity electrode, the correlation between weakened adhesion strength and improved lithium ion migration by electrolyte absorption has to be investigated further.

The electrochemical characteristics of binders were examined via EIS, CV, and coin-half cell tests. Fig. 1(a) shows the effect of binder MW on the EIS of graphite electrodes. By comparing the semicircle size in the medium frequency region, it is clear that the electrodes containing high MW PVA binders have higher charge transfer resistance than those containing low MW PVA. With increasing MW of PVA, more clustered structures are formed with the active materials and a larger amount of binder is located on the surface of active materials by strong hydrogen bonds. Additionally, the high MW PVAs absorbed less electrolytes, leading to difficulty in lithium ion movement. These are why the high MW PVA showed larger charge transfer resistances. From the CV results of a very thin PVA45 film and the PVA-containing electrode, even though these are not shown, the PVA binder was confirmed electrochemically stable in the working voltage.

The charge/discharge results of graphite electrodes are displayed in Fig. 1(b). All of the PVA-containing electrodes except for PVA35 showed higher capacity than the PVDF-containing electrode, though there is not much difference among the binders. To investigate the effect of binder on high capacity anodes, we chose PVA45 and PVA50, which showed better capacity retention in the graphite electrode, as binders for Si/graphite electrodes. Also, two different MWs of both PVDF and PAA were used as binders and were compared with the PVA binders. As shown in Fig. 1(c), the discharge capacity of PVDF-containing electrodes abruptly drops after the 4th cycle regardless of MW of PVDF binders. It is clear from Fig. 1(d) that this drop is due to delamination of the electrodes from the current collector due to the low adhesion strength of PVDF binders. On the other hand, increases in MW of PVA and PAA binders improved cyclic performance of high capacity anodes, as expected. The PAA-containing electrodes showed much better cyclic capacity retention than PVDF-containing electrodes, even though their adhesion strengths were as low as the PVDF electrodes. This may be attributed to stronger hydrogen bonding between carboxylic groups in PAA and active materials as well as

Table 1

Material properties of synthesized PVA polymers, the adhesion strength(AS) of electrodes, and the electrolyte swelling ratio of polymer films.

	PVA35	PVA40	PVA45	PVA50	PVDF-L	PVDF-H	PAA-L	PAA-H
DP of PVAc (n)	37705	41248	42359	35927	–	–	–	–
DS(%)	93.65	91.06	94.00	94.86	–	–	–	–
AS of C electrode(g _f /cm)	114.9 ± 32.1	119.5 ± 19.5	139.4 ± 10.1	106.5 ± 11.6	1.4 ± 1.0	–	–	–
AS of Si/C electrode(g _f /cm)	–	–	111.0 ± 29.0	70.6 ± 28.9	4.8 ± 3.4	13.6 ± 2.5	8.6 ± 3.2	6.3 ± 4.2
Swelling after 48 hr (%)	33.3	28.6	31.8	45.8	44.5	–	–	–

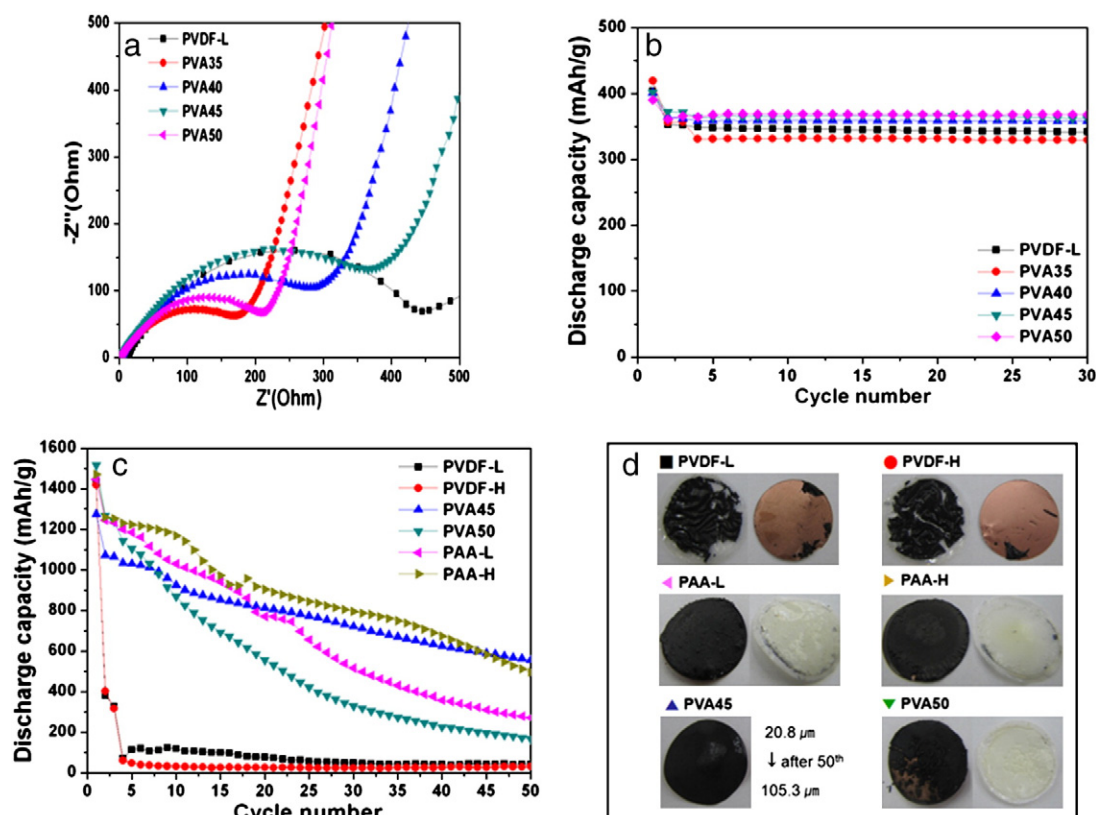


Fig. 1. (a) EIS of graphite electrodes, (b) cycling performance of graphite electrodes, and (c) cycling performance of Si/graphite electrodes. Pictures of Si/graphite electrodes in (d) were taken after 50 discharge/charge cycles.

current collectors than the hydrogen bonding in PVDF electrodes. Unlike the PVDF electrodes, the hydrogen bonds in PAA electrodes remain during cycling tests and keep the electrodes attached to the current collector as displayed in Fig. 1(d). As the cycle proceeds, however, a large stress is built up in the electrode due to its volumetric expansion/contraction [14], and ultimately radial cracks appear to release the stress from the outside of the electrode, as shown in the picture of the PAA-H electrode. This leads to a steady decrease in the capacity of the electrode.

In the case of the PVA45 electrode, the strong hydrogen bonding of PVA is enough to prevent the electrode from radial cracking. Instead, all of the volumetric change occurs in the axial direction. After the 50th cycle, the thickness of the electrode was approximately 5 times larger than that of the fresh electrode. This is much larger than the theoretical value of 1.98. Thus, it is expected that lots of space was created inside the electrode during the intercalation/deintercalation processes. By modifying Si/C composites, this space could be reduced and the cyclic performance could be much better than the experiments shown in Fig. 1(c).

4. Conclusion

It has been proven for the first time that high MW PVA could be a novel binder for high capacity anodes due to the strong hydrogen bonds between the hydroxyl groups in PVA and active materials as well as the current collector. By combining technology to manufacture

high capacity active materials the PVA binder will significantly enhance the electrochemical properties of high capacity anodes.

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