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Influence of polymer binder structure on the properties of the graphite anode for lithium-ion batteries

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ABSTRACT

This paper discusses the impact of the structure and properties of three different polymer binders: polyvinylidene fluoride, sodium carboxymethyl cellulose and polyvinyl alcohol, on the electrochemical properties of spherical graphite anodes for Li-ion batteries. Electrochemical tests indicate that the nature of polyvinylidene fluoride contributes in decreasing the cycle life of graphite electrodes in contrast to effective water-based binders. This study demonstrates the possibility of manufacturing graphite-based electrode for Li-ion batteries that cycle longer and use water in the processing, instead of hazardous organic solvents like N-methylpyrrolidone, thereby improving performance, reducing cost and protecting the environment.

1. Introduction

In lithium-ion batteries production process, a polymer binder has a very important function, namely binding the active materials of the electrode in one conductive mass. The adhesive and chemical properties of the binder have a great impact on the performance of the battery. Over the past 20 years, during which lithium-ion batteries have become increasingly popular, major research effort has been focused on materials for this type of batteries, like anodic and cathodic active materials, separators and electrolytes, which have been extensively studied from year to year and in the case of which tremendous progress has been achieved [1-3].

The most conventional binder used for composite electrodes for lithium-ion batteries is polyvinylidene fluoride (PVdF). PVdF may have superior chemical and electrochemical stability, but this does not entirely eliminate Li-ion battery producers' problems such as having to use toxic organic solvents such as N-methylpyrrolidone (NMP), which are indispensable for dissolving polymer. In addition, the cost of PVdF-based electrodes is still a concern in the battery industry [4-8]. What is more, PVdF also tends to swell in organic

solvents, which can lead to the active mass breaking away from the electrode current collector during battery work [1]. Thus, a large amount of effort has been put into the creation of an environment-friendly and cost-effective binder for lithium-ion batteries. Extensive research has been conducted into in this field, such as carboxymethyl cellulose (CMC), mainly as its sodium neutralized derivative, and polyacrylic acid (PAAH) [8-11]. Recently, some new kinds of binders have been tested for lithium-ion batteries, for example acrylate polymers, such as polyacrylic acid (PAA) containing carboxyl groups maintain excellent cyclic retention for C-Si-based electrode materials thanks to hydrogen bonding. Among them polyvinyl alcohol (PVA) has received considerable attention because it contains numerous hydroxyl groups in its structure which can increase cohesion between active materials and a current collector [12-19]. The chemical structure of PVA is shown in Figure 1, along with PVdF and CMC structure for comparison.

In this study, aqueous-based PVA and CMC binders and organic-based PVdF for spherical structure graphite (MCMB) electrodes were investigated. The physical and chemical properties of the pristine binders were researched. Then MCMB-based anodes with different binders were prepared to

examine the effect of water-based binders on electrochemical characteristics which were compared with the PVdF based binder system.
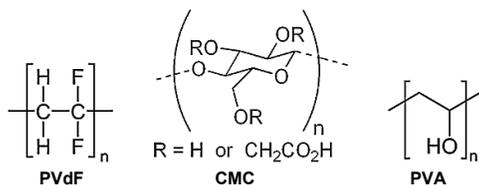

Figure 1. Chemical Structure of PVdF, CMC, PVA.

2. Experimental

Three kinds of polymer binders were used to prepare anodes: PVdF powder (M_w = ~530000 g/mol), purchased from Fluka, sodium carboxymethyl cellulose (CMC, M_w = ~700000 g/mol) from Aldrich and PVA (M_w = 85-124000 g/mol) supplied by Aldrich. All binder powders were characterized by scanning electron microscopy (SEM, Quanta FEG 250 Scanning Electron Microscope). The X-ray powder diffraction patterns of the samples were taken by means of Philips PW1050 diffractometer, with Ni filtered CuKα. Structural analysis was carried out using ATR-FT-IR spectrometer (Bruker, TENSOR 27) and solubility tests were done.

The commercial anode active material MCMB (MesoCarbon MicroBeads Graphite) was provided by MTI Corporation. Super C65 conductive carbon black was acquired from Timcal Graphite & Carbon. The graphite MCMB was characterized by scanning electron microscopy (SEM, Quanta FEG 250 Scanning Electron Microscope) and a detailed specification was conducted to determine the specific surface area using ASAP 2010M.

To study the effect of different polymer binders on electrochemical performance of the MCMB anodes in lithium ion batteries, PVdF, CMC, PVA were utilized to prepare anodes consisting of MCMB and C-65 in a weight ratio of 10:80:10, with suitable amounts of solvent (NMP for PVdF, deionized water for CMC, PVA, respectively). The obtained slurries were coated onto Cu foil and dried at 120 °C for 24 h under vacuum. Swelling properties of the electrodes were tested by soaking them in the electrolyte for 48h and calculating the difference in mass. Electrochemical measurements were performed by using Swagelok-type half-cells. The carbon electrode was used as a work electrode. Lithium metal was used as a counter electrode and a reference electrode and Celgard 2400 (poly(ethylene) foil, Celgard) as a separator. The electrolyte was LP30 (mixture of ethylene carbonate (EC) and ethylmethylcarbonate (EMC) in volume ratio of EC:DMC (1:1) with 1 M lithium hexafluorophosphate ($LiPF_6$), Merck). All the operations on the cells assembled were carried out in a glove-box filled with argon gas. The cells were galvanostatically discharged to 0.01 V and charged to 2.0 V at the rate of 30 or 50 mA per gram of active mass in 10 cycles and 150 mA/g in 100 cycles. Galvanostatic experiments were performed using multichannel potentiostat/galvanostat Atlas 0461 (Atlas-Sollich, ZSE).

3. Results and discussion

Infrared spectroscopy was used to characterize the chain structure of polymers employed to prepare anode electrodes. Figure 2 displays the ATR-FT-IR spectra of the PVA, CMC and PVdF binders.

For PVA binder, the main absorbance band at 3000-3600 cm^{-1} verified the presence of a hydroxyl group -OH and C-O bonding in the region of 1000-1250 cm^{-1}. Also, the peak at around 2850-2900 cm^{-1} on IR curve of PVA was an indication of CH/CH$_2$ bonding. For CMC binder, the peaks of sodium

carboxylate group at 1600 and 1420 cm^{-1} could be observed. Additionally, small vibrational bands in the range 900-1100 cm^{-1} observed in the pattern were attributed to the ether groups from cellulose [15,18]. For PVdF binder the vibrational bands at 890 and ~1200 cm^{-1}, were ascribed to the stretching frequencies of CF$_2$. Crystallization peaks which were assigned to the vibration of the crystallization PVdF according to Peng's report [17,21] were observed at range 600-900 cm^{-1}. The crystallinities of the binders were examined by X-ray diffraction. Figure 3 presents X-ray diffraction patterns of the three binders.
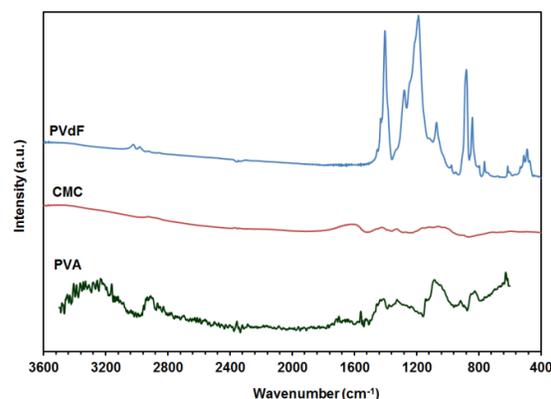

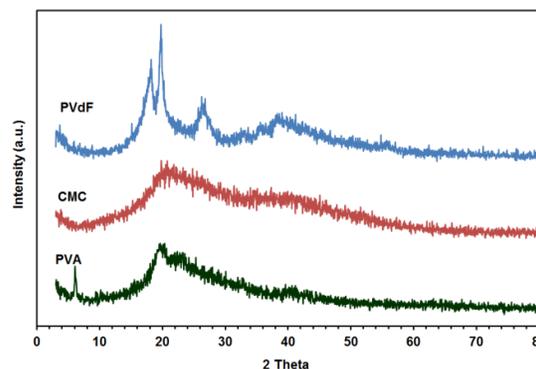**Figure 2.** ATR-FT-IR analysis of PVdF, CMC and PVA binder.

Figure 3. X-ray diffraction patterns of the three binders.

X-ray diffraction analysis showed characteristic reflection peaks at 2θ (2Θ) for all polymers, where the peak for PVdF was much sharper than for the other two polymers. According to Han's report [15,20], we probably observed the conse-quences of a higher degree of PVdF crystallinity structure than CMC and PVA, which is known as a semicrystalline polymer. This conclusion can also be confirmed by the SEM images of the three binder pristine solid powders (Figure 4).

The spherical structure of the grains of PVdF with tendency to create occlusive agglomerates was observed. This spherical, regular shape of particles is one of the features of crystal. For CMC and PVA, we observed only an irregular shape of particles, which confirmed their rather amorphous character. These differences in the structural of polymers may greatly influence the morphologies of polymer films formed after being dissolved in solvent and dried in the next step during the preparation of the electrode. Because of the semicrystaline structure of the PVdF, we can expect numerous pores in the film of this polymer and, consequently, the structure of electrode with this kind of binder having numerous pores in contrast to amorphous polymer-based films like CMC or very low crystallite PVA [17, 23-25].
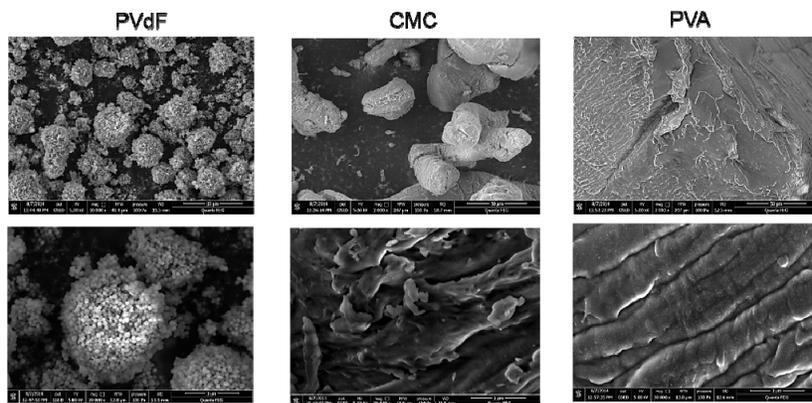
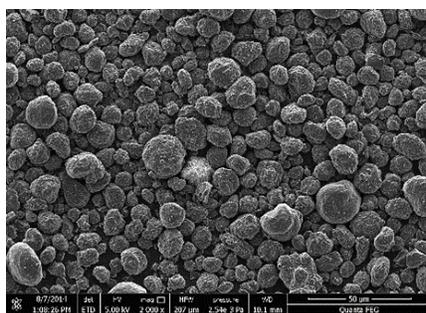**Figure 4.** SEM images of PVdF, CMC, PVA pristine solid powders, respectively.
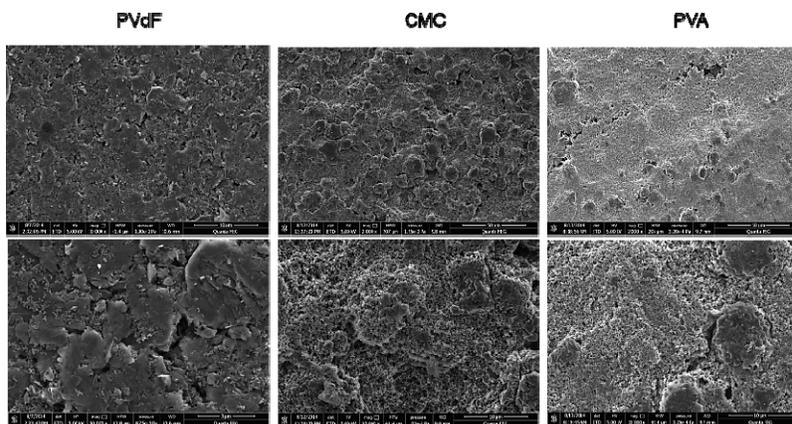

Figure 5. SEM images of MCMB graphite powder.

Figure 6. SEM images of the MCMB electrodes with three different polymeric binders.

A typical SEM image of the MCMB graphite particles is shown in Figure 5. We can notice the spherical microbead shaped particles of this graphite. During ASAP analysis specific data of this material were collected. The specific surface area (BET) of the MCMB graphite stands at 1.54 m^2/g, total pore volume 2.11 cm^3/g and average particle size of the graphite's grains is 10 μm.

The morphology of the electrodes in this study was characterized by using SEM mapping techniques. Figure 6 shows the SEM images of MCMB-based electrodes with different polymer binders. Composite structure of the electrodes was observed, where the spherical structure of graphite was the most visible in comparison with water-based binders composite electrodes. Electrodes for the preparation

of which PVdF binder was used have shown a very homogenous structure.

Swelling properties of the electrodes were examined by soaking them in the electrolyte LP30 solution at room temperature for 48 h. After that time, the electrodes were taken out to weigh the mass (m_1) after removing the electrolyte on the surface with the filter paper. The initial weight of the electrodes before test was letter m_0. The increased mass percentage of the polymer films was calculated according to the equation: (m_1-m_0)/m_0. The differences in mass of electrodes before and after contact with liquid electrolyte were between 2-3% of their mass, similar to all three binders. Probably 10% of the binder provides enough adhesion to prevent the electrode from decomposing after being in contact with the electrolyte for 48 hours.

Table 1. Basic electrochemical parameters of the graphite anodes in the examined cells determined on the galvanostatic charge/discharge experiments: Q_{1ch}-charge capacity in the 1st cycle, Q_{1dis}- discharge capacity in the 1st cycle, Q_{irr}- irreversible capacity ($Q_{irr} = Q_{1ch}-Q_{1dis}$), Eff- coulombic efficiency of charging in the 1st cycle.

Polymer binder in electrode	Current density of cycling (mAg^{-1})	Q_{1ch} (mAhg^{-1})	Q_{1dis} (mAhg^{-1})	Q_{irr} (mAhg^{-1})	Eff. (%)
PVdF	30/50/150	504/485/413	326/322/339	178/163/74	54/51/82
CMC	30/50/150	377/334/172	354/303/161	23/31/11	94/91/94
PVA	30/50/150	410/444/178	306/284/130	104/160/48	75/64/73

Another experiment regarding swelling was performed by soaking the three different binders directly in the liquid electrolyte, simulating a similar condition as inside a lithium-ion battery. Figure 7 records the beginning and the end situation (after 48 h).

Before soaking in LP30   After 24 h soaking in LP30
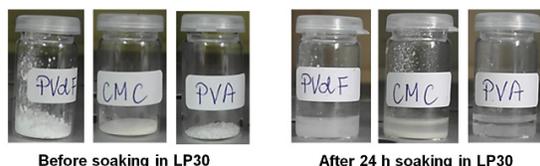
Figure 7. Swelling properties of the polymer binders in contact to liquid electrolyte.

PVdF powder easily swelled, forming a viscous, gel-like fluid product, which was in accordance with other reports [17,26-27]. PVA swells but only in small proportions. In contrast, CMC, a water-based binder, does not swell in the same experimental conditions in contact with liquid electrolyte. The swelling of binders is one of the most important factors for reversible cycling of the electrode in a battery. PVdF-based electrodes seem to be the most unstable during long cycling, which was confirmed during our experimental work. The half-cells with graphite electrodes were cycled galvanostatically at: 30 and 50 mA/g in 10 cycles and 150 mA/g in 100 cycles in 25 °C. Galvanostatic charge/discharge tests have shown how and how long lithium ions have been reversibly intercalated into MCMB-based graphite electrodes and what the highest value of the capacity is for this kind of electrode materials depending on the binder's structure. Table 1 summarizes numerical electrochemical data calculated on the basis of galvanostatic characteristics.

Importantly, graphite anode charged/discharged in electrode with water-based binders exhibits a smaller value of irreversible capacity in the first cycle for all cycling tests in contrast to electrodes with PVdF. It is probably due to construction of the electrodes, where surfaces of electrodes with PVA and CMC are much more heterogeneous in comparison with PVdF-based electrodes. Consequently, the working surface area of the electrode is a little bit more expanded but, most importantly, water based binders do not dissolve in electrolyte in contrast to PVdF.

Nevertheless, numerical data in Table 1 indicate that in the first cycle for all cycling the both Q_{1ch} and Q_{1dis} values are higher for MCMB electrodes with PVdF. These dependencies are true for the studied systems up to 10 cycles. In systems cycling over 10 times an opposite trend can be observed (Figure 8).

Discharge capacity over 10th cycle up to 100th is higher for electrodes with water-based binders (ca. 270 mAh/g). In the case of Q_{dis} for electrodes with PVdF we observe a decrease as the number of charge/discharge cycles increases. In the 100th cycle Q_{dis} is equal to ca. 150 mAh/g for this type of electrodes, which is almost twice as low as in the 1st cycle. It may suggest that after about 10 cycles during the test with current density 150 mA/g the PVdF based graphite electrode is decomposed to quite a large extent. What is more, after cycling tests, the PVdF composite electrode could be detached from the cuprum current collector easily, while the other electrodes with CMC and PVA binders tightly stuck to the current collectors, as can be seen in Figure 9.

This evidence also supports our conclusion that the graphite electrodes with water based binders like CMC and PVA have better physical and electrochemical stability.
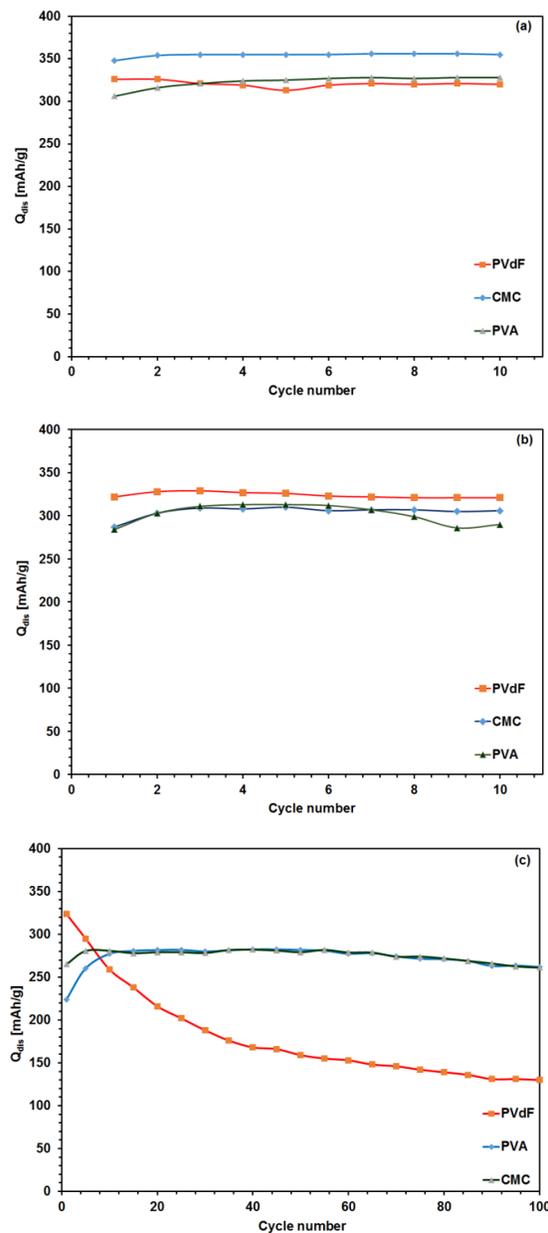
Figure 8. The cycling properties of MCMB electrodes prepared using PVdF, CMC and PVA as a binder: (a) current density: 30 mA/g, (b) current density: 50 mA/g, (c) current density: 150 mA/g.

Figure 9. Pictures of graphite electrodes after 100 charge/discharge cycles (current density 150 mA/g).

4. Conclusion

The paper describes how the water-based binders (CMC and PVA) were applied as effective binders for graphite anode with MCMB for Li-ion batteries in comparison with the organic solvent-based binder PVdF.

Based on this study, the following conclusions can be drawn:

- The surface of graphite electrodes with MCMB shows a higher homogeneity level for compounds prepared with water based CMC and PVA polymers, compared with compounds with PVdF polymer dissolved in organic solvents. The surface of the electrodes with CMC and PVA is much higher than that of electrodes with PVdF.
- The structure of polymer binders and their ability to swell in liquid electrolyte highly influences the mechanical properties of graphite electrodes, especially the adhesion strength between active materials and the current collector. During research work the most satisfying adhesion was observed for all graphite electrodes with water- based binders: CMC and PVA.
- The influence of the binder structure on the electrochemical properties of electrodes is considerable. For anode half cells with MCMB graphite and investigated binders, the reversible capacity value in the first cycles is satisfying for electrodes based on PVdF, and is almost comparable with the theoretical value of graphite capacity, what is more, the PVdF-based electrodes with MCMB graphite show higher capacity in the anode half cells with researched graphite electrodes up to 10 cycles. After about 10 cycles of charging and discharging with current density 150 mA/g discharge capacity for electrode mass drops drastically. This happens because the electrode mass separates from the current collector, as it is laminated with PVdF based electrode mass, prone to swelling in a liquid electrolyte, which results in decreasing adhesion.

Acknowledgement

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