



Improved Mechanical and Electrochemical Properties of Artificial Graphite Anode Using Water-Based Binders in Lithium-Ion Batteries

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In recent years, many studies have focused on the active materials of anodes to improve the performance of LIBs, while limited attention has been given to polymer binders, which act as inactive ingredients. However, polymer binders have amazing influence on the electrochemical performance of anodes. Herein, to investigate the binding performance between MCMB artificial graphite and the copper current collector, three binders such as PVDF, MSBR, and CMC+SBR were used to prepare the anode electrodes. The mechanical and electrochemical tests were conducted for different MCMB electrodes. The results show that the water-based binders (CMC+SBR and MSBR) made better adhesion properties for the coating on the current collector in comparison with the organic solvent-based binder (PVDF). MCMB anode fabricated with CMC+SBR binder shows the highest discharge capacity and the best rate performance at various C-rates of 0.2C, 0.5C, and 1C that result in the brilliant electrochemical performance. Therefore, artificial graphite anode materials using cheap aqueous CMC+SBR binder instead of toxic solvent like NMP and expensive PVDF improve electrochemical property and reduce the cost of LIBs.

1. INTRODUCTION

Population growth, industrial development, and increased fossil fuel consumption have intensified the energy crisis and environmental pollution, which is becoming a major issue for many cities [1-4]. As one of the great potential solutions to ameliorate energy crisis and environmental pollution, electric vehicles (EVs) are being widely developed all over the world. Lithium-ion batteries (LIBs) are being progressively used in EVs, because of their high energy density, low self-discharge, long cycle life, and no memory effect [5-7].

Carbon materials have received much attention as anode material for LIBs since 1990. Different carbon materials have been studied and shown good performances as the host for lithium. They have high reversible capacity, high charge/discharge efficiency, long cycling life, and low electrochemical potential [8, 9]. Mesocarbon Microbeads (MCMB) prepared from petroleum pitch or coal tar are one of the candidate carbon materials available commercially. MCMB can be easy for close packing, because it has a spherical structure that results in high density of electrode. Its low surface area can also minimize the side reactions during charge/discharge process. Enormous studies have been focused on the active materials of anodes to improve the performance of LIBs, while limited attention has been given to polymer binders, which act as "inactive" ingredients [10, 11]. The role of binders in composite electrodes is providing mechanical stability and surface adhesion of the coating to the current collector [12]. In the last research, polymer binders have been attracting more attention for their amazing influence on the electrochemical performance of carbon anodes [13, 14].

Polyvinylidene fluoride (PVDF) is known as a traditional binder that involves the use of N-methyl pyrrolidone (NMP) in its processing, which is toxic and environmentally harmful [15]. In the last few years, water soluble polymers have received attention to improve the electrochemical performance of anode electrodes in LIBs. For example, carboxymethyl cellulose (CMC) [16, 17], styrene butadiene rubber (SBR) [18], polyvinyl alcohol (PVA) [19, 20], and polyethylene glycol (PEG) have used water instead of NMP.

The weak van der Waals force between PVDF and active particles usually fails to bind particles strongly to maintain the electrode integrity when active electrode materials undergo a huge volume change, leading to a severe capacity fading [21]. To lighten this problem, polymers containing carboxylic groups such as CMC are adopted as binders because they can improve the formation of a stable solid electrolyte interphase (SEI) film and accommodate the volume change of active particles [22]. In addition, PVDF reacts with lithiated graphite and Li, which leads to the peeling of the electrode particles and, consequently, capacity fading [23].

Electrodes made with CMC+SBR mixtures displayed lower first cycle irreversible capacity loss than PVDF-based electrodes [24, 25], which is attributed to a faster formation of SEI induced by the interactions between carbon and CMC [25]. It is recognized that the presence of hydroxyl and carboxyl functions is the key feature responsible for the improved electrochemical performance. CMC readily reacts with the electrolyte upon simple soaking (prior to cycling), generating a protective surface layer composed of R-O-PF₄ and LiF [26].

Herein, to investigate the binding performance between MCMB and the copper current collector, three binders such as PVDF, modified SBR (MSBR), and CMC+SBR were used to prepare the anode electrodes. The mechanical and electrochemical tests were done for various MCMB

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electrodes. The results indicate that CMC+SBR binder was more suitable for making MCMB anodes of LIBs.

2. EXPERIMENTAL

2.1. Materials

Three kinds of polymer binders were used to prepare anode slurry: PVDF powder, SBR emulsion + CMC purchased from Gelon LIB Group, and modified SBR emulsion from Targray.

MCMB (Gelon) with an average diameter (d_{50}) of 16.5-19 μm , a specific surface area of less than 1.5 m^2/g , and a tap density of more than 1.28 g/cm^3 were used as the active ingredient of the anode slurries. Carbon black (Super P Li, Gelon) with a density of 160 kg/m^3 was added as a conductivity agent.

2.2. Electrodes preparation

Table 1 presents a composition of MCMB anodes with different binders. To prepare the anode electrodes, active and conductive materials were heated in vacuum oven for 2 hours at 120 $^{\circ}\text{C}$. The CMC and PVDF binder were dissolved respectively in distilled water and NMP and, then, were stirred for 24h at ambient temperature. Afterwards, the active material (MCMB) and conductivity agent (CB) were dry mixed using mortar and gradually added to the different three binder solutions. This mixture was further mixed and degased with vacuum-mixer at a rate of 100 rpm for 1h to create a homogenous dispersion before coating the slurry on the copper foil (99.99 % purity, thickness 9 μm , MTI Corporation). Once the slurry was prepared, it was coated on copper foil using a doctor-blade method.

After drying overnight at 60 $^{\circ}\text{C}$ in vacuum oven, the electrodes were pressed using roll press to ensure good contact between the electrode components, as well as between the electrode mass and the current collector. Then, electrode disks were punched (diameter: 14 mm) from the electrode sheet. The disks were dried in vacuum oven at 60 $^{\circ}\text{C}$ for 2 hours before cell assembly.

Table 1. Composition of MCMB anodes with different binders.

Electrode	E1	E2	E3
MCMB	94.5 %	94.5 %	94.5 %
CB	1 %	1 %	1 %
SBR	2.25 %	-	-
CMC	2.25 %	-	-
MSBR	-	4.5 %	-
PVDF	-	-	4.5 %

*All on dry weight

2.3. Cell assembly

The two-electrode CR2032 coin-type half-cells were assembled in a glove box with both moisture and oxygen level below 0.5 ppm. A porous polymer film (thickness: 25 μm) was used as the separator. The electrolyte was 1 M LiPF_6 solution in a mixture of EC/DEC (1:1) (MTI Corporation). A Li-metal foil with 16 mm diameter and 0.6 mm thickness (Gelon LIB Group) was used as counter and reference electrodes. Finally, the cells were sealed by electric coin cell crimping machine (MTI Corporation). After assembly, the cells were kept at rest for 3 hours to ensure complete percolation of electrolyte through the electrode and membrane pores.

2.4. Characterization

In order to quantify the adhesion strength of porous coatings on copper foil, a tensile strength tester (Gotech) was used. An electrode with a defined surface area was fixed between two parallel plates using double-sided adhesive tape, as shown in Figure 1. At first, a pre-compression load of 20 Kg.f was applied to achieve a reproducible adhesive bond between electrode and compression grips. Then, the grips were gotten apart with a speed of 5 mm/min. The measured tensile stress was defined as adhesion strength.

In order to evaluate the electrochemical performance, all cells were charged and discharged by a battery testing system (Neware technology ltd.) at various rates of 0.2C, 0.5C, 1C, and 0.2C under a cutoff potential range of 0.01–2.0 V. All electrochemical experiments were carried out at ambient temperature.

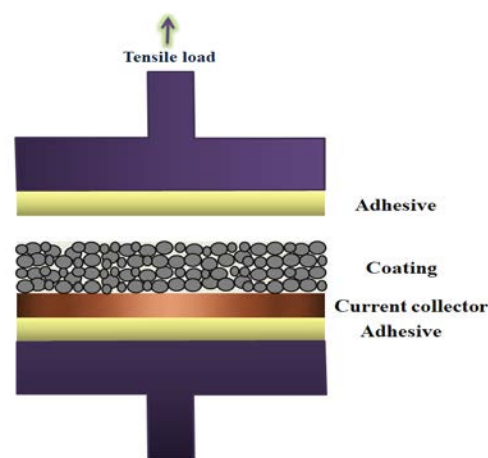


Figure 1. Mechanism of adhesion strength test.

Electrochemical impedance spectroscopy (EIS) tests were conducted in the frequency range of 10 mHz-100 kHz (the applied bias voltage was set at open circuit voltage). The formation of SEI film was investigated by impedance spectra recorded after charge/discharge cycles. The experimental Nyquist plots were simulated by an equivalent electronic circuit using the fit and the simulation options in the frequency response analyzer (FRA) of the NOVA software.

3. RESULTS AND DISCUSSION

3.1. Mechanical properties

Figure 2 represents the adhesion strength of MCMB anodes prepared with different binders. The anodes prepared with CMC+SBR, MSBR, and PVDF show 2.070, 2.013, and 1.376 MPa adhesion strength, respectively. Therefore, the water-based binders (CMC+SBR and MSBR) made better adhesion properties for the coating on the current collector in comparison with the organic solvent-based binder (PVDF).

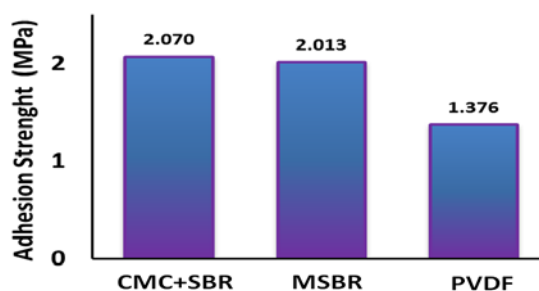


Figure 2. Adhesion strength of MCMB anodes prepared with different binders.

As shown in Figure 3, there are three failure mechanisms that can be related to the coating:

- Interface failure (between adhesive and coating).

- Cohesion failure (failure within coating).
- Adhesion failure (between coating and current collector).

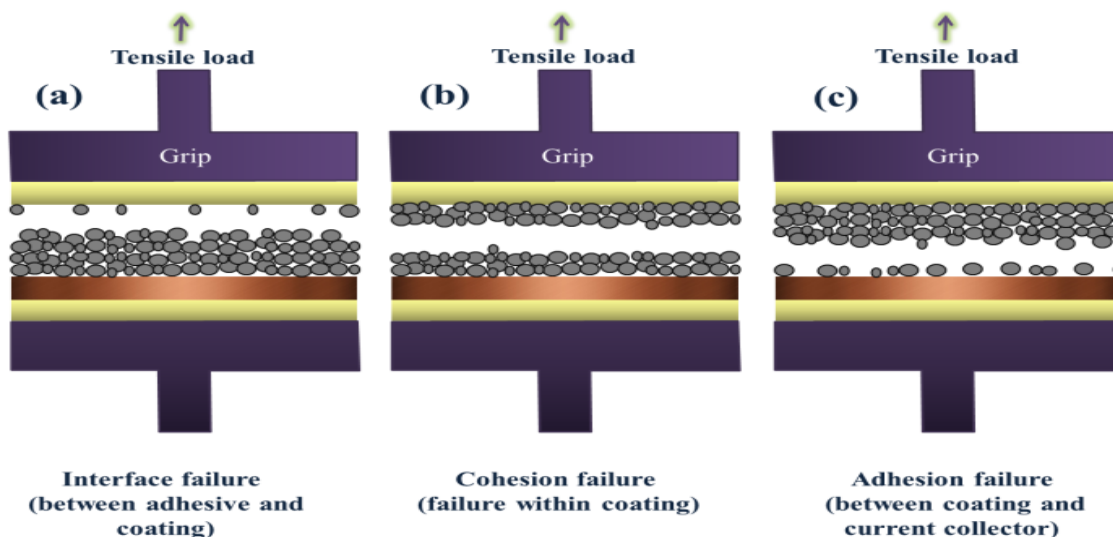


Figure 3. Failure mechanisms of coating after adhesion strength test.

Figure 4 illustrates the electrode surfaces after the adhesion test. According to Figures 3-a and 4-a, interface failure occurs for MCMB anode prepared with CMC+SBR, which indicates the strongest adhesion and cohesion properties in MCMB electrode. In the case of MSBR (Figures 3-b and 4-b), a cohesion failure occurs so that the adhesion strength between the active material coating and the current collector is more than the cohesion strength within the coating. According to the failure mechanism for PVDF (Figure 3-c), a poor adhesion strength observed for the PVDF-containing coating is probably a mixture of adhesion and cohesion failure (Figure 4-c). It means that the adhesion strength between the active material coating and the current collector is lower than the cohesion strength within the coating; thus, an adhesion failure occurs for PVDF.

As CMC+SBR shows the best mechanical properties in MCMB anodes, it can improve the mass loading of the electrode that influences the energy density of a battery cell for a specific application (e.g., high power or high energy cells).

3.2. Electrochemical performance

The charge/discharge cycling performance of MCMB anodes was investigated in different C-rates, and the results are shown in Figure 5. Before cycling, pre-cycling at a rate of 0.1C for 1 cycle was carried out to form a stable SEI layer on the surface of MCMB particles for the following charge/discharge cycles. The half-cells were cycled five times at each C-rate: 0.2C, 0.5C, 1C, and then back at 0.2C. The charge/discharge profiles of the tested MCMB anodes at different C-rates of 0.2C, 0.5C, and 1C (the fifth cycle of each C-rate) are shown in Figure 6.

As shown in Figure 5 and Figure 6-a, at 0.2C CMC+SBR shows the highest discharge capacity of 315.6 mAh/g, followed by MSBR and finally PVDF, which showed capacities of 312.9 and 305.4 mAh/g.

By increasing the C-rate up to 0.5C (Figure 6-b), CMC+SBR still shows a capacity of 316.4 mAh/g. At 0.5C, the capacity of MSBR is 309.6 mAh/g, and PVDF binder shows a capacity of 295.6 mAh/g (97 % of the capacity at

0.2C). At 1C (Figure 6-c), capacities are severely reduced down to 290.3 mAh/g for MSBR, which represents 92.7 % of the capacity observed at 0.2C, and down to 281.8 mAh/g for PVDF, which indicates 92.3 % of the capacity observed at 0.2C. However, CMC+SBR still shows an almost stable capacity of 314.2 mAh/g at 1C. When the MCMB half-cells were cycled back at 0.2C (Figure 5), the ones prepared with CMC+SBR and MSBR showed a total recovery of the capacity: 315.7 mAh/g and 303.8 mAh/g, respectively. In the case of PVDF, a large capacity loss of 18 % is observed that can be attributed to its poor mechanical properties.

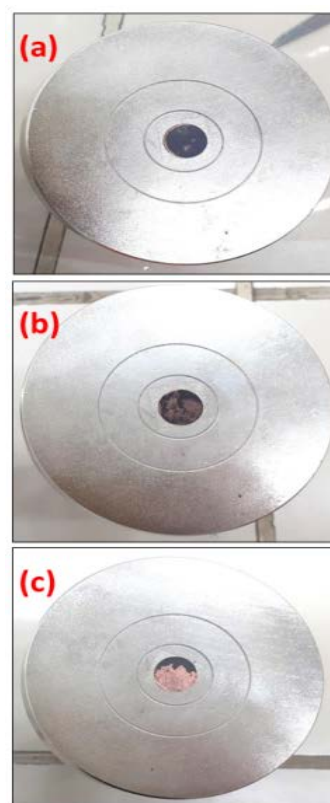


Figure 4. Surface of MCMB electrodes using different binders after the adhesion test: (a) CMC+SBR, (b) MSBR and (c) PVDF.

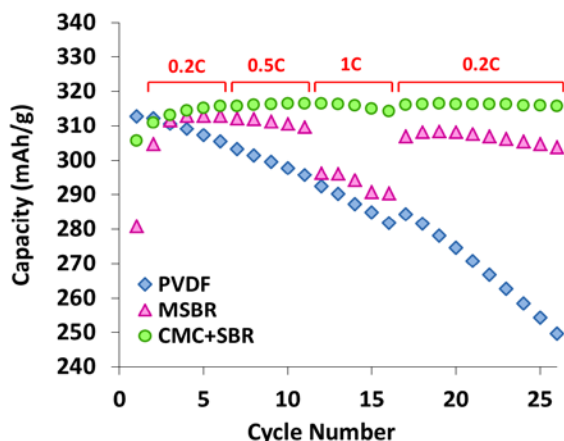


Figure 5. Rate performances of the MCMB electrodes prepared with different binders.

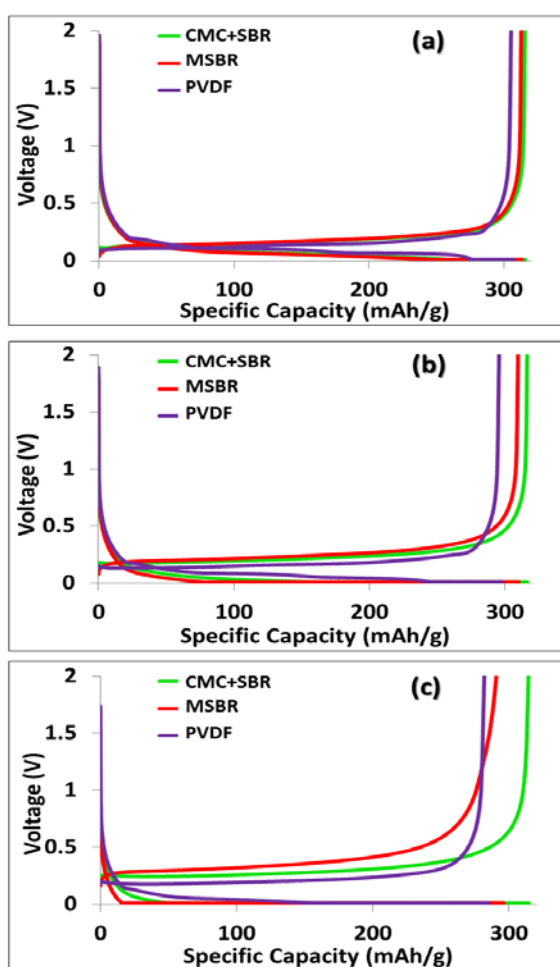


Figure 6. Voltage profile of MCMB anodes at different C-rates of (a) 0.2C, (b) 0.5C, and (c) 1C.

Figure 7 shows the Nyquist plots from half cells of MCMB anodes prepared with various binders after cycling at different C-rates. Each electrochemical impedance spectrum contains two semicircles, which can be simulated by an equivalent circuit (Figure 8-a). The resistance of R_s indicates the bulk electrolyte resistance, and the observed semicircle at high frequency is considered as the resistance of SEI film (R_{SEI}). The medium-frequency semicircle represents the charge-transfer resistance (R_{ct}) of the intercalation process between the electrodes and the electrolyte. Other elements of CPE_{SEI} and CPE_{ct} are constant phase elements associated with R_{SEI}

and R_{ct} , respectively. The slope at the low frequency is attributed to Warburg impedance, which shows the diffusion process of Li^+ ion in the electrolyte-electrode interface. Table 2 presents the simulation results obtained from EIS data of various MCMB anodes prepared with different binders. Figure 8-b represents a comparison of R_{SEI} for three MCMB electrodes. The value of R_{SEI} is 24.7Ω for PVDF, which is larger than that of MSBR (6.25Ω) and CMC+SBR (2.84Ω). Therefore, after charge/discharge cycling at different C-rates, the MCMB electrode using CMC+SBR binder has the smallest resistance of SEI film, which provides the best cycling performance for this electrode.

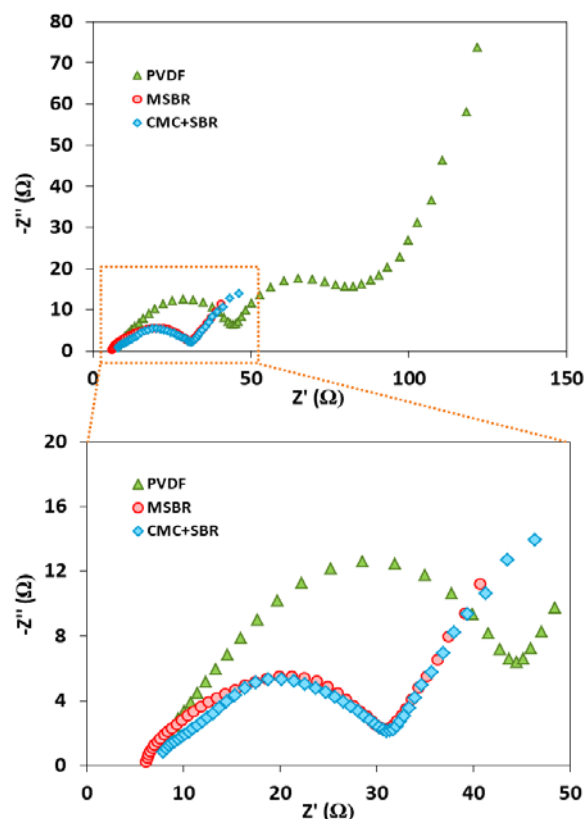


Figure 7. Nyquist plots of MCMB anodes prepared with PVDF, MSBR, and CMC+SBR binders after cycling at different C-rates.

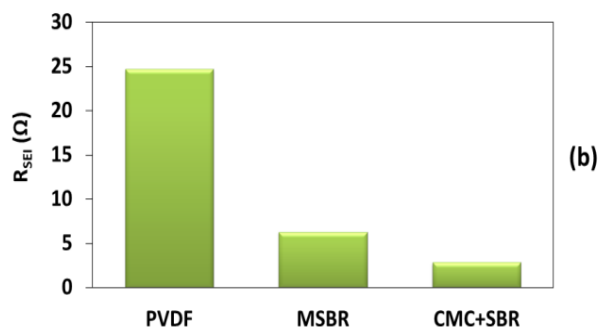
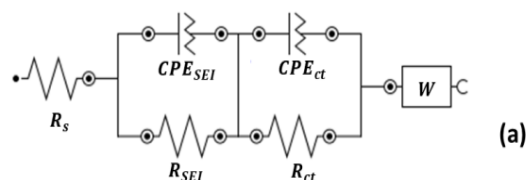


Figure 8. (a) The equivalent circuit used to simulate the impedance spectra and (b) Comparison of the values of R_{SEI} for MCMB anodes prepared with different binders.

Table 2. Simulation results obtained from EIS data of different MCMB anodes prepared with PVDF, MSBR, and CMC+SBR binders.

Binder	R_s (Ω)	R_{SEI} (Ω)	CPE_{SEI}		R_{ct}	CPE_{ct}		W (mMho)
			Y_o (μ Mho)	N		Y_o (mMho)	N	
PVDF	7.85	24.7	2780	1.03	39.6	0.11	0.665	45.9
MSBR	5.98	6.25	475	0.622	17.9	1.61	0.64	268
CMC+SBR	7.36	2.84	73.5	0.722	20.2	0.92	0.597	189

4. CONCLUSIONS

Three polymer binders of PVDF, MSBR, and CMC+SBR were prepared and used in MCMB artificial graphite anode. The mechanical and electrochemical tests were done for various MCMB electrodes. The results indicated that the water-based binders (CMC+SBR and MSBR) made better adhesion properties for the coating on the current collector in comparison with the organic solvent-based binder (PVDF). According to obtained results, CMC+SBR made the strongest adhesion and cohesion properties in MCMB electrode. In contrast, a poor adhesion strength observed for the PVDF-containing coating is probably a mixture of adhesion and cohesion failure. MCMB anode fabricated with CMC+SBR binder showed the highest discharge capacity and the best rate performance at various C-rates of 0.2C, 0.5C, and 1C that result in the brilliant electrochemical performance. Therefore, LIBs anode materials using cheap aqueous CMC+SBR binder instead of toxic solvent like NMP and expensive PVDF improve the electrochemical property and reduce the cost of LIB.

5. ACKNOWLEDGEMENT

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