

Fabrication of petroleum pitch/polymer composite binder for anode material in lithium-ion battery

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Abstract : The lithium ion battery has applied to various fields of energy storage systems such as electric vehicle and potable electronic devices in terms of high energy density and long-life cycle. Despite of various research on the electrode and electrolyte materials, there is a lack of research for investigating of the binding materials to replace polymer based binder. In this study, we have investigated petroleum pitch/polymer composite with various ratios between petroleum pitch and polymer in order to optimize the electrochemical and physical performance of the lithium-ion battery based on petroleum pitch/polymer composite binder. The electrochemical and physical performances of the petroleum pitch/polymer composite binder based lithium-ion battery were evaluated by using a charge/discharge test, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and universal testing machine (UTM). As a result, the petroleum pitch(MP-50)/polymer(PVDF) composite (5:5 wt % ratio) binder based lithium-ion battery showed 1.29 gf mm⁻¹ of adhesion strength with 144 mAh g⁻¹ of specific dis-charge capacity and 93.1 % of initial coulombic efficiency(ICE) value.

Keywords : Petroleum pitch, conventional polymer based binder, petroleum pitch/polymer composite, lithium ion battery.

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1. Introduction

The increase in use of fossil fuels such as coal, fossil oil and natural gas bring a huge amount of substances that cause environmental pollution and global warming [1]. In order to overcome these issues, development of the progressive technology and intelligent materials on energy sources such as lithium-ion batteries (LIBs) are required, where the batteries should have high electrochemical performances including volumetric and gravimetric energy density with sufficient safety [2].

Various research has been investigated to develop active materials of anodes to enhance the performance of LIBs, while there was lack of attention to binders which is providing mechanical stability and adhesion between coating of electrode material and current collector [3]. Polyvinylidene fluoride (PVdF), carboxymethyl cellulose (CMC), styrene butadiene rubber (SBR), polyvinyl alcohol (PVA) and polyethylene glycol (PEG) are well known conventional polymer based binder which also involve the use of organic solvents including N-methyl pyrrolidone (NMP) and water [4]. Even though PVdF is the most widely used binder for LIBs, it exhibits limitation such as, it shows weak Van der Waals force between binders and active material which can decrease electrochemical performance of LIBs by volume change of the electrode material during charge/discharge process [5]. In addition, CMC/SBR mixture based binder shows lower irreversible capacity at first charge/discharge cycle than PVdF binder based electrode [6]. As a result, investigation of binding materials to replace conventional polymer based binder is needed to improve physical and electrochemical performances of the LIBs.

Carbon materials have received great attention to use as anode material for LIBs since 1990 due to their high charge/discharge efficiency, high reversible capacity and long life

cycle [7, 8]. Petroleum pitch based mesocarbon materials are one of the suitable materials to the LIBs electrode and they are available commercially [8]. It also shows the efficient charge/discharge process by spherical structure that would minimize the side reaction on the charge/discharge process with high density of electrode [9, 10]. The coal-tar pitch based electrode materials are also widely conducted to fabricate the anode for lithium-ion battery. However, it requires process optimization to control the chemically complicated polyaromatic hydrocarbons (PAHs) and impurities such as metal oxides and sulfur lead to capacity fading [11]. On the other hand, petroleum pitch is synthesized and polymerized from the petroleum residue (PFO) oil according to various thermal reactions [12]. Petroleum pitch has also enriched functional groups with high purity compared to coal-tar residue which could also affect the physical and electrochemical performances of the LIBs. In addition, petroleum pitch has sp² hybridized carbon atoms with abundant aromatic hydrocarbons which are showing similar to hexagonal ranged carbon atoms in graphene which could be improved physical and electrochemical performances of the lithium-ion battery [13–15].

In this study, the petroleum mesophase pitch as a MP-50 was introduced to fabricate petroleum pitch/polymer composite and used as a binder to the anode of LIBs. We have also optimized petroleum pitch/polymer composite binder to maximize physical and electrochemical properties of the LIBs. The electrochemical and physical properties of petroleum pitch/polymer composite binder based LIBs were evaluated via cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), charge/discharge test and universal testing machine (UTM). The obtained experimental data in this work suggested that petroleum pitch based binder could be replaced to the polymer based conventional binder in

LIBs and improved its electrochemical and physical performances.

2. Experimental

2.1. Material

Polyvinylidene fluorine (PVdF, #9300, KUREHA Corporation, Japan) was purchased to use as a binder to prepare electrode. Petroleum pitch (MP-50, 50% of isotropic contents), was obtained from Korea Research Institute of Chemical Technology (KRICT) and used to fabricate petroleum pitch/polymer composite as a binder. N-methyl-2-pyrrolidone (NMP) was purchased from Sigma-Aldrich and used as a solvent without any purification. The LiCoO_2 (LCO) was purchased from COSMO AM&T CO and used as an active material of the electrode. Carbon black (Super-P) was obtained from Imerys Graphite to use as a conducting additive in the electrode.

2.2. Synthesis of petroleum pitch (MP-50)

PFO (pyrolysis fuel oil, LG Chem, Ltd, Korea) was a byproduct of NCC (naphtha cracking center) and used without any purification to synthesis petroleum pitch. 1800 g of PFO was feeding to reactor, and reaction temperature was set to $420\text{ }^\circ\text{C}$ for 180 min at normal pressure. The heating rate was $2.0\text{ }^\circ\text{C min}^{-1}$, and the flow rate of nitrogen gas fed 200 cc/min to ensure an inert condition. Figure 1 is illustrated that process of synthesizing for petroleum pitch (MP-50, 50% of isotropic contents).

2.3. Preparation of petroleum pitch(MP-50)/polymer composite binder

The petroleum pitch/polymer composited binder was fabricated by using simple technique with petroleum pitch (MP-50), PVdF and NMP. Briefly, 10 wt% concentration of PVdF dispersion was prepared by using NMP as a solvent. Then, MP-50 was added to the PVdF dispersion to create petroleum pitch/polymer composite with vigorous stirring over the 12

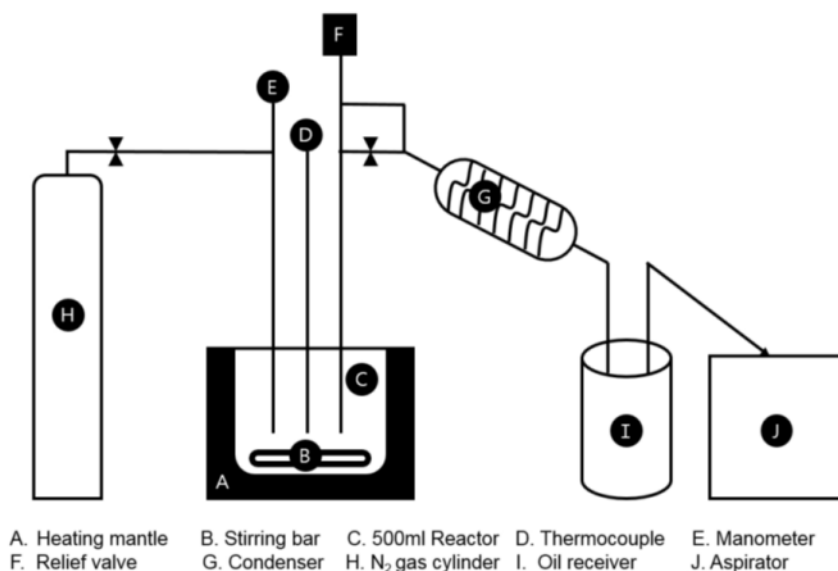


Fig. 1. Scheme of the reactor system for synthesis of petroleum pitch.

hrs at room temperature. The various ratio between PVdF and MP-50 were carried out to optimize its physical and electrochemical properties of the petroleum pitch/polymer composite binder based lithium-ion battery (see the Table 1.)

2.4. Preparation of the cathod materials slurry

The electrode slurry was prepared by mixing with LiCoO_2 (LCO), Super-P and MP-50/PVdF composite binder in NMP [16]. The mass ratio of electrode slurry was 96 (LCO): 1 (Super-P): 3 (MP-50/PVdF composite binder) and mixed by thinky mixer at 1500 rpm for 30 min. The LCO and Super-P should be mixed in a bowl in advance to enhance dispersability in the electrode slurry. After that the prepared slurry was coated with 0.035 mm of thickness on the current collector (aluminum foil) by using doctor blade method and dried for overnight in vacuum oven at 120 °C to remove residual solvent.

2.4. Fabrication of petroleum pitch(MP-50)/polymer composite binder based lithium ion battery

The fabricated electrode was punched to 14 π of diameter and its thickness (0.28 mm) and density (1.6 g/cm^3) were measured. 1.3 M LiPF_6 in ethylene carbonate (EC) / ethyl methyl carbonate (EMC) / dimethyl carbonate (DMC) (3/4/3, v/v, ENCHEM, Korea) was

used for the liquid electrolyte and the separator was cut into the 18 π of diameter. The lithium-ion battery (coin half-cell) was assembled in argon-filled glovebox ($\text{H}_2\text{O} < 1 \text{ ppm}$, $\text{O}_2 < 1 \text{ ppm}$). Lithium-ion battery was manufactured with standard CR 2032 coin-cell hardware, consisted of the cathode, lithium metal anode and separator.

2.5. Physical properties of the petroleum pitch(MP-50)/polymer composite binder based lithium ion battery

The effect of carbonization of the PFO and petroleum pitch (MP-50, 50% of isotropic contents) was evaluated by using FT-IR (Perkin Elmer, Frontier, USA) analyzer. The sample was scanned from 4000 to 500 cm^{-1} of wavenumber. The orientation of petroleum pitch (MP-50, 50% of isotropic contents) was observed using polarized optical microscopy (Olympus BX43, Japan). MP-50 was inserted in epoxy resin and polished using Struers Tegramin-25. After that, the sample was observed at 40 \times magnification using an Olympus BX43 microscope.

The measurement technique (ASTM D3330) was conducted to evaluate the adhesion strength between electrode coating and current collector by using the universal testing machine (KUTM-TB, Korea). The peel test tape was attached to mid-plane of the electrode coating and its size should be 25 mm. Adhesion strength could be performed by peeling the

Table 1. The various mass ratio of the MP-50/PVdF composite binder

Ratio (MP-50/PVdF, w/w%)	Petroleum pitch (MP-50, g)	PVdF (g)	NMP (g)
Neat PVdF	1	0	9
7/3	0.7	0.3	9
5/5	0.5	0.5	9
3/7	0.3	0.7	9
0/10	0	1	9

tape off the 180° upright substrate.

2.6. Electrochemical properties of the petroleum pitch(MP-50)/polymer composite binder based lithium ion battery

Cyclic voltammetry (CV) measurements of lithium-ion battery based on the petroleum pitch/polymer composite binder was performed with ZIVE BP2A electrochemical workstation (ZIVE-LAB, WonATech, Korea). All the measurements were recorded by scan rate of 10 mVs⁻¹ with potential range 3.0 V to 4.5 V at room temperature. The charge/discharge test of lithium-ion battery based on the petroleum pitch/polymer composite binder was conducted by using ZIVE BP2A electrochemical workstation (ZIVE-LAB, WonATech, Korea). The lithium-ion battery was charged and discharged from 3.0 V to 4.3 V with a constant C-rate of C/10 (0.1C) [17]. The cycle test was applied to 10 hrs after performing of the charge/discharge test by using ZIVE BP2A electrochemical workstation (ZIVE-LAB, WonATech, Korea). The upper cutoff voltage limit was set at 4.3 V, and the discharge voltage limit was set to 3.0 V. Electrochemical impedance spectroscopy (EIS) was carried out to prove the electro-chemical behavior between the electrode and electrolyte interface. EIS measurements were performed at room temperature via ZIVE BP2A electrochemical workstation (ZIVE-LAB, WonATech, Korea) where the frequency ranges from 100 kHz to 0.01 Hz with an amplitude of 1 mV [18].

3. Results and discussion

The Fourier-transform infrared spectroscopy (FT-IR) was performed to characterize the effect of carbonization PFO and the results demonstrated in Figure 2. In the FT-IR spectra, the PFO and the petroleum pitch

showed peaks at 1420–1330 cm⁻¹ and 840–790 cm⁻¹, which present aliphatic CH₃ bonding and C–C stretching, respectively [19]. In addition, the peaks of aliphatic C–H stretching (2018–2954 cm⁻¹) was measured in the petroleum pitch. The peak intensity about aromatic and aliphatic on petroleum pitch was in-cresed after carbonization of PFO, which might be due to the increase of C–C structure and decrease of impurity amounts. [20].

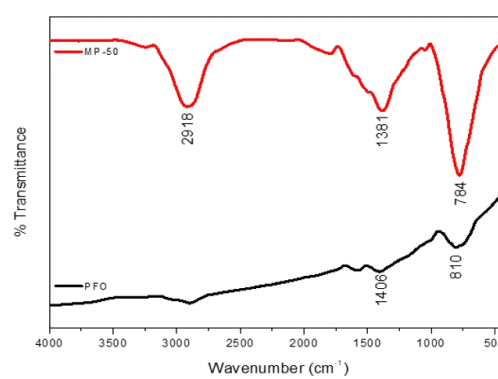


Fig. 2. Fourier transform infrared (FT-IR) spectra of the petroleum residue and pitch.

The adhesion strength as a physical performance between current collector and electrode is a critical factor for high capacity of the active materials and would reduce significant volume change during the charge/discharge process [21]. Figure 2 gave the adhesion strength of electrodes based on various ratios of MP-50/PVdF composite binder based electrodes. The adhesion strength of the electrodes based on neat PVdF (10 wt%) binder was 37.8 ± 0.5 (mean ± S.D., n=10 devices) gf mm⁻¹ and MP-50/PVdF (5/5 wt% ratio) composite binder based electrode exhibited 1.29 ± 0.28 (mean ± S.D., n=10 devices) gf mm⁻¹ of adhesion strength. The adhesion strength of electrode based on the MP-50/PVdF composite binder was increased with respect to increase mass

ratio of PVdF in the composite [22]. It might be due to the higher adhesion strength of the neat PVdF than MP-50/PVdF composite samples, which also corresponding with Figure 3.

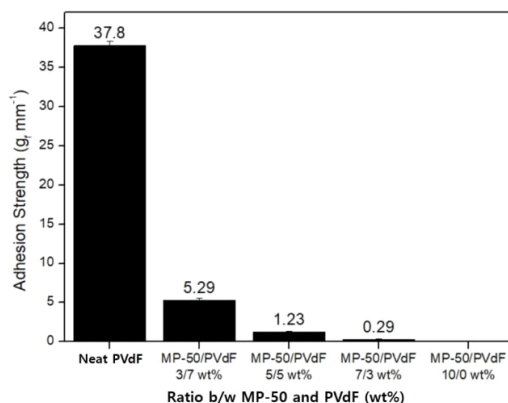


Fig. 3. Typical adhesion strength measurement value with various ratio of petroleum pitch/polymer composite binder.

The electrochemical performance tests were carried out to optimize ratio between petroleum pitch (MP-50) and polymer (PVdF). The electrochemical performances of the lithium-ion battery based on various ratio of the MP-50/PVdF composite binder were illustrated in Figure 4. In the case of the neat MP-50 binder based lithium-ion battery could not fabricate due to the electrode material was broke and separated from current collector by brittle property of the petroleum pitch. In Figure 4 a, the lithium-ion battery based on the neat PVdF (10 wt% ratio) binder showed 155 mAh g⁻¹ of initial specific charge capacity with 144 mAh g⁻¹ of the initial specific discharge capacity at a C/10 rate. On the other hand, the lithium-ion battery based on the MP-50/PVdF (5/5 wt% ratio) composite binder maintained stable specific discharge capacity of 144 mAh g⁻¹ at 3 - 4.3 V with 93.1 % of ICE value. This result implied possibility that petroleum pitch could

replace conventional polymer based binder with maintain its electrochemical performance. However, the electrochemical performances of the MP-50/PVdF composite binder based lithium-ion battery were decreased with respect to increase contents of petroleum pitch (MP-50) in the binder composite. Especially, the MP-50/PVdF (7/3 wt% ratio) composite binder based lithium-ion battery figured out a very low ICE value of 80 % with 122 mAh g⁻¹ of specific discharge capacity value. In addition, decreasing of the specific discharge capacity and overcharged were observed with respect to increase of the MP-50 contents in the binder composite. It might be due to the laminate form of the electrode and decreased stability and utility of the active material by adding of the MP-50 as the petroleum pitch in the binder composite [23]. Figure 4 b illustrated the cycling performances with various ratio of the MP-50/PVdF composite binder based lithium ion battery. The lithium ion battery based on the neat PVdF (10 wt%) binder exhibited higher specific discharge capacity of 189 mAh g⁻¹ when compared to the lithium-ion battery based on the MP-50/PVdF (3/7, 5/5 and 7/3 wt% ratio) composite binder. The lithium-ion battery based on the MP-50/PVdF (3/7 wt% ratio) composite binder maintained 52% of its initial specific discharge capacity and the MP-50/PVdF (5/5 wt% ratio) composite binder based lithium-ion battery showed 41 % of retention value even after 100 cycles.

In contrast, the discharge capacity of the lithium-ion battery based on the MP-50/PVdF composite binder was decreased with respect to increase discharge cycles at all the samples. This results also in accordance with morphology study of the electrode as the Figure 5 a~d. In Figure 5 d, a crack appeared on the surface of electrode after application of 100 cycles which could lead to irreversible lithium ions and finally decrease electrochemical performances and electrical conductivity

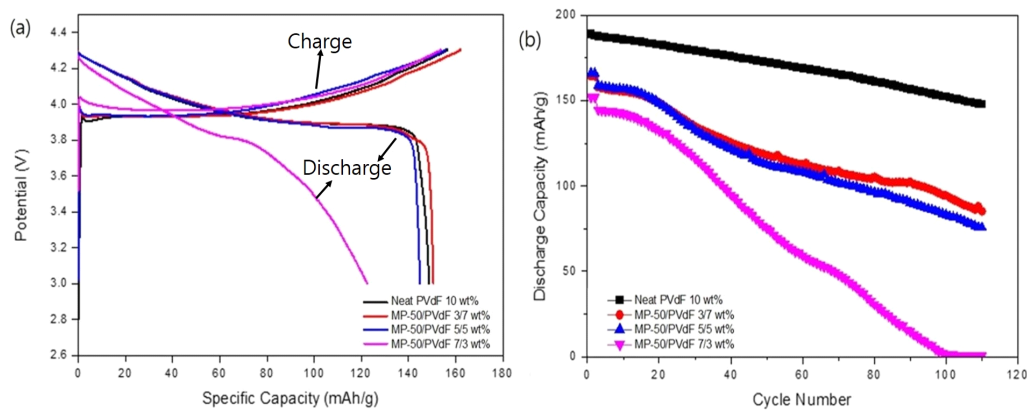


Fig. 4. Electrochemical properties of the lithium ion battery based petroleum pitch/polymer composite binder (a) charge/discharge profiles (b) cycle life span.

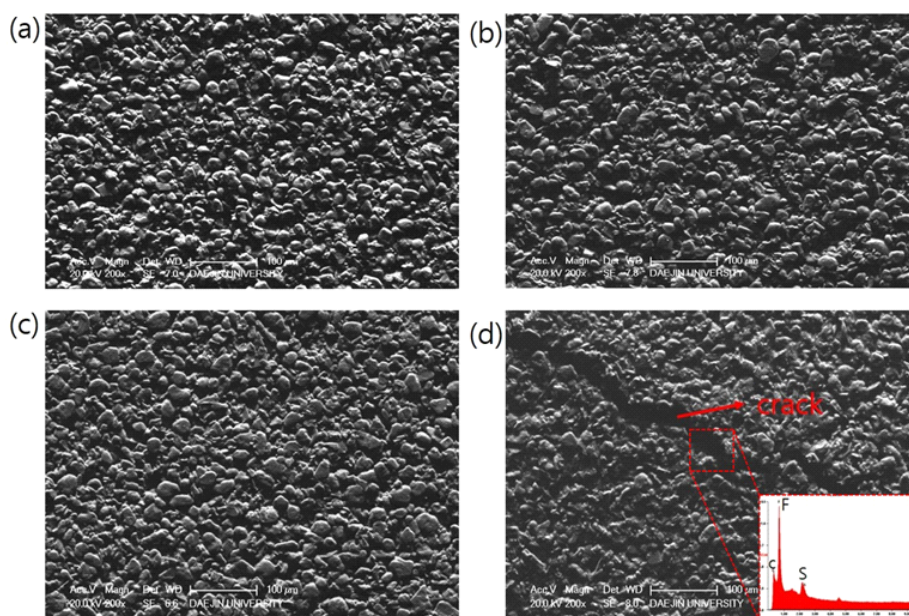


Fig. 5. Scanning Electron Microscope (SEM) images of the (a, c) neat PVdF binder based electrode, (b, d) MP-50/PVdF (5/5 wt% ratio) composite based electrode

of the petroleum pitch based lithium-ion battery [24, 25].

Figure 6 a demonstrated the cyclic voltammetry (CV) curves of the lithium-ion battery based on various ratio of the

MP-50/PVdF composite binder. Lithium-ion battery based on the neat PVdF (10 wt%) binder exhibited a pair of oxidation (3.92 V) and reduction peaks (3.38 V) on the curves, which is the largest oxidation and reduction

peaks area, indicated the highest capacitance value [26]. The oxidation peak shifted to high voltage range (to the right) with decrease PVdF contents in the MP-50/PVdF composite due to the intermediate stage of redox reaction could be occurred in high voltage range [27]. Figure 6 b gave the Nyquist plots of the lithium ion battery based on various ratio of the MP-50/PVdF composite binders. In the Nyquist plots, R_s represented solution resistance that depends on the electrolyte solution between electrodes. R_{ct} , C and Z_w indicated charge transfer resistance, double layer resistance and Warburg impedance, respectively [28]. The lithium-ion battery based on the neat PVdF (10 wt%) binder showed the largest area of semicircle which indicated the high transfer resistance between electrode and electrolyte. The transfer resistance was increased with respect to increase of the MP-50 contents in the binder composite. It seems that the contents of petroleum pitch would affect to increase the transfer resistance which also would be interrupted ions moving and activity between electrode and electrolyte interfaces [29]. The result of initial resistance value of the lithium-ion battery based on various ratio of the MP-50/PVdF composite binder are shown in Table 2. The initial resistance was also increased with increase of the MP-50 contents in the binder composite, however, there is no significant difference within 2Ω . Therefore, it seemed that the contents of MP-50 as the petroleum pitch would not have a significant effect on the resistance value of the electrodes [30].

4. Conclusion

In this study, we have introduced MP-50 as the petroleum pitch to use as a binding material to replace conventional polymer based binder in the lithium-ion battery. The ratio

between MP-50 and PVdF was also optimized to increase electrochemical and physical performances of the petroleum pitch/polymer composite binder based lithium-ion battery. The lithium-ion battery based on the MP-50/PVdF composite binder (5/5 wt% ratio) showed high specific discharge capacity value of 144 mAh g^{-1} . In the cycling performance, the retention rate was decreased with respect to increase the mass ratio of the MP-50 in the binder composite. In the Nyquist plots, the neat PVdF binder (10 wt% ratio) based lithium-ion battery gave the lowest initial resistance value with the largest semicircle area. It is noted that the contents of the MP-50 as the petroleum pitch would not effect on the initial resistance of the lithium-ion battery based on MP-50/PVdF composite binder. The lithium-ion battery based on the MP-50/PVdF composite binder showed low electrochemical performances with respect to increase of the petroleum pitch contents in the binder composition. This research has significant finding that the previous studies have not been investigated lithium-ion battery on the petroleum pitch in binding materials and shown possibility to replace conventional polymer based binder.

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