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

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Experimental

Methacrylic acid, and triethylene glycol methacrylate were obtained from Sigma-Aldrich and purified using a basic Al_2O_3 column to remove the stabilizer. A CGP-G8 graphite (from ConocoPhillips) was used as the anode material. Battery-grade acetylene black (AB) with an average particle size of 40 nm was acquired from Denka Singapore Private Ltd. N-methylpyrrolidone (NMP) was purchased from Aldrich chemical company. The slurries containing 87% graphite, 10% binder, and 3% acetylene black in NMP solvent were prepared. The slurry was homogenized by using a Polytron PT10-3S homogenizer at 4000 rpm for 30 min until viscous and uniform slurry was obtained. Electrode laminates were prepared by casting the slurries onto copper foil by doctor blade method. All the electrode films were cast to have approximately the same loading of active material (around 30-46µm). All the electrode laminates were dried at 130 °C for 16 h under vacuum before use. 2325 coin cell was assembled using Celgard 2400 separator, the electrolyte is 1.0 M lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate (EC)/diethylcarbonate (DEC) (1/1 weight ratio, BASF) and lithium as the counter electrode to make half cells. The assembled coin cells were tested using Maccor battery cycler Seires 4000 at 30 ^{o}C in a thermo chamber, with a cut-off voltage of 0.01V~1V, a theoretical capacity of 310 mAh/g was used to calculate the C rate.

A Bruker Biospin Advance II 500 MHz Nuclear Magnetic Resonance (NMR) spectrometer was used to collect the proton and carbon NMR spectra of the synthesized products. The Differential Scanning Calorimetry (DSC) was performed using Perkin-Elmer Diamond DSC, with a heating rate of 10 ^{o}C/min from 30 ^{o}C to 250 ^{o}C. The molecular weight of polymer was determined by use of an Agilent 1200 Series HPLC equipped with a refractive index detector. A PLgel 10-µm miniMIX-B 250 × 4.6 mm column (Varian, Inc.) was employed with dimethylformamide (DMF) eluent (0.3 mL/min) and calibrated by using PEO standard samples (Agilent Technologies) in DMF. The polymer binder was coated on Cu foil for a Cyclic Voltammetry (CV) test. CV and Electrochemical Impedance Spectroscopy (EIS) were conducted on a VMP galvanostat/potentiostat (Bio-Logic), while CV was characterized with a potential of 10 mV and a cycling rate of 0.1 mV/s. Graphite half cells were cycled for one cycle at a C/25 rate, lithiated for 12.5 hours at a C/25 rate, and rested for 4 hours before EIS measurement. The sample cells were brought to 10 mV before impedance measurement was taken at 0.01 Hz to 0.1 MHz. The graphite electrode was prepared by coating a copper foil current collector with a slurry of CGP-G8 and different binders *N*-methyl-2-pyrrolidone (NMP), the electrodes were dried at 130 ^{o}C for 12 h in a vacuum oven.

To do the electrolyte uptake test, polymer is made into a round disk with a diameter of 2.2 cm and thickness of 1 mm. The polymer sample was weighed and immersed into the electrolyte (EC/DEC=1, 1M LiPF6) for 48 hours before taking out and measure the weight again. Morphology of the electrode surface was characterized using a JSM-7500F scanning electron microscope (SEM). After cycling, the graphite electrodes were washed with dimethyl carbonate (DMC) solvent inside an argon-filled glove box to remove residual electrolyte. A homemade transfer system equipped with a gate valve and a magnetic manipulator was used for transfer of the highly sensitive samples from the pure argon atmosphere of the glove box to the SEM system. Fourier transform infrared spectroscopy (FTIR) was performed in a Varian 3100 FT-IR Excalibur Series.

The microscratch test was performed by scratching the electrode surface with a tip using a CETR Tribometer (Bruker Inc.). a conical diamond stylus with a tip radius of 1.5 µm and a cone angle of 60^o was used. The micro-indenter tip was drawn over the electrode surface and a 2 mm long scratch track was made by translating the sample while linearly ramping up the normal load on the conical tip from 6 mN to 50 mN. Adhesion measurements of graphite electrode were performed on a Chatillon® TCD225 series force measurement system. The Cu side of graphite electrode (1 cm × 1 cm) was fixed vertically to the bottom sample holder. The adhesive side of a Scotch Magic® tape was firmly applied onto the electrode laminate side. The Scotch Magic® tape was peeled of using the top sample holder at the direction of 180^o angle to the adhered tape and parallel to one side of the graphite electrode, and at 10 inch min^{-1} moving rate to the bottom sample holder. A layer of the graphite laminate was peeled off and adhered to the moving scotch magic tape. The force required to peel of the laminate was recorded as indication of the adhesion between the binder and graphite materials. The first data point of each test, between 0 and 0.05 cm, corresponds to the beginning of the tape tension, with the forced offset to zero. When the tension is fully applied and the electrode laminate is peeled off, the measured force value reaches a plateau, representing the adhesion force of the electrode laminates.

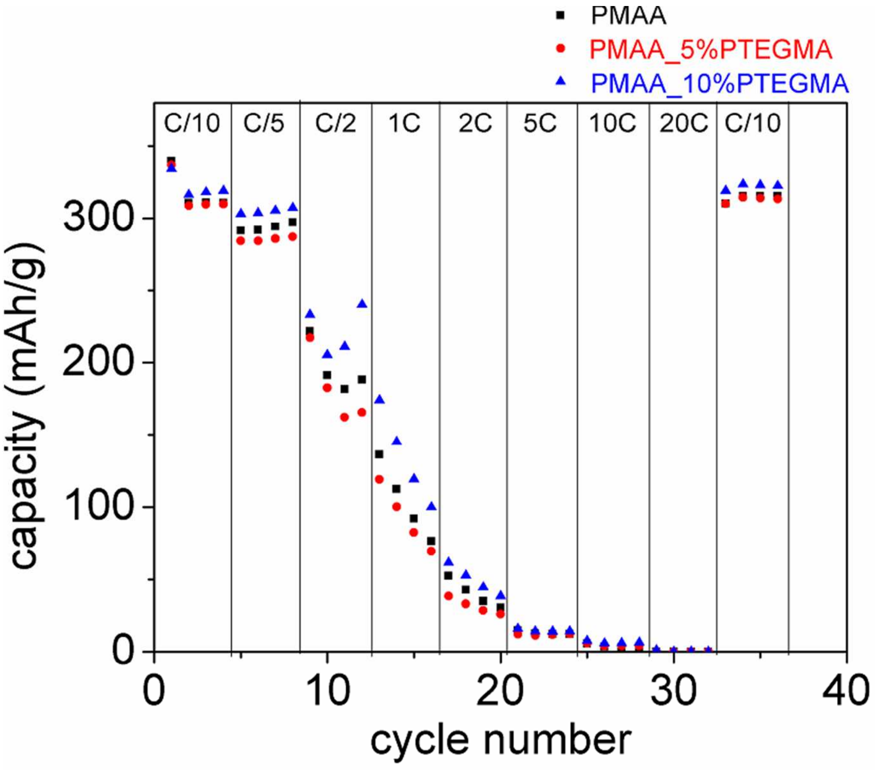

Figure S1. The rate performance of the graphite anodes with (a) PMAA, (b) PMAA-5%PTEGMA, and (d) PMAA-10%PTEGMA.

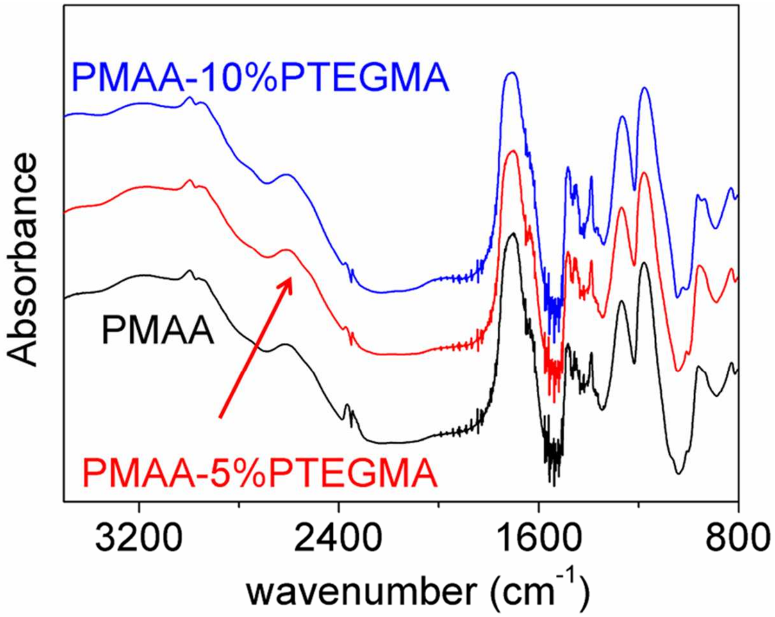

Figure S2. FTIR of the three PMAA-based polymer binders.

The FTIR spectra of the synthesized PMAA-based polymers are presented in Figure 1b. The strong peaks in the 1800~1600 cm^{-1} region are assigned to the carbonyl group in either PMAA or PTEGMA structure. The signals at ~3000 cm^{-1} corresponds to the acidic proton in the carboxylic acid groups of PMAA. Comparing the three spectra, no big difference is observed, probably due to the small amount of PTEGMA incorporated into the polymer.