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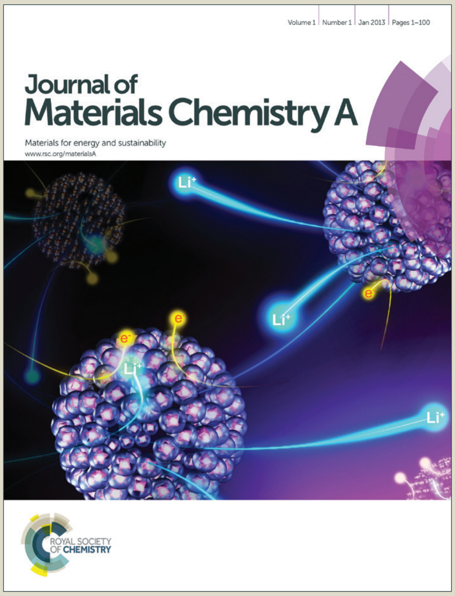

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# Flexible Fluorine Containing Ionic Binders to Mitigate the Negative Impact Caused by The Drastic Volume Fluctuation from Silicon Nano-Particles in High Capacity Anodes of Lithium-Ion Battery

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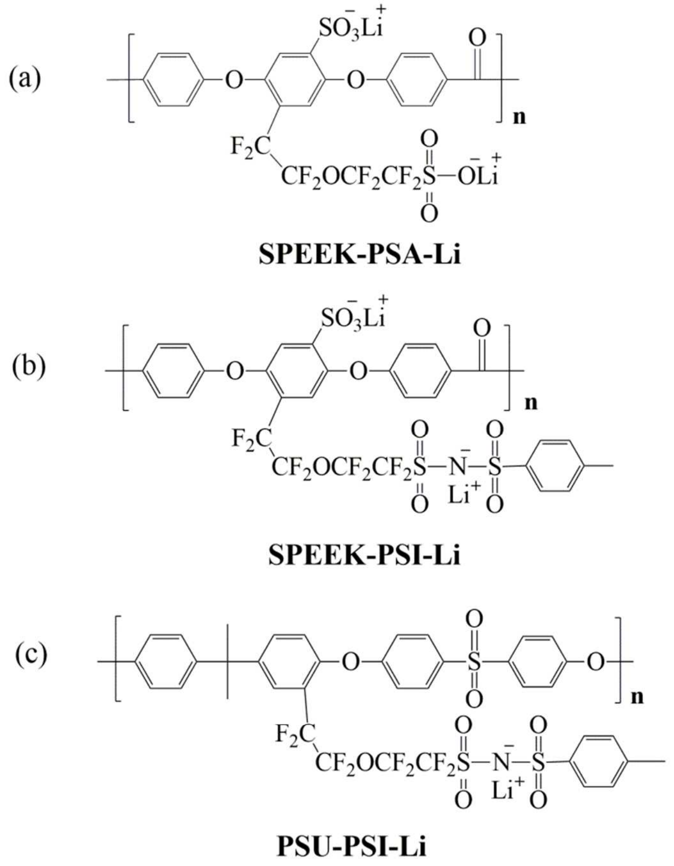
Novel ionic binders based on sulfonated polyether ether ketones and polysulfone backbones, bearing pendant lithiated fluorinated sulfonimide groups (SPEEK-PSI-Li and PSU-PSI-Li) were developed. Their performance in high performance silicon (Si) nano-particles anodes were studied in comparison with conventional binders such as lithiated sulfonated poly(ether-ether-ketone) containing fluorinated sulfonic acid side chains (SPEEK-PSA-Li), poly(vinylidene) difluoride (PVDF), sodium carboxymethyl cellulose (CMC) and alginate. Much superior to other anode binders, the ionic conducting SPEEK-PSI-Li binders could not only provide good adhesion property, but also effectively reduce the over-potential during rapid charge and discharge cycles. When cycled at a current of 400 mA g$^{-1}$, these anodes could maintain above 2000 mAh g$^{-1}$ after 50 cycles. Even cycled at a high current rate of 2000 mA g$^{-1}$, the anodes with SPEEK-PSI-Li binders could be cycled above 500 mAh g$^{-1}$ in 50 cycles. The superior performance of the novel SPEEK-PSI-Li binders could be attributed to their high cohesion capability, low solubility in electrolyte, high adaptability to volume fluctuation and high ionic conducting capability resulting from of the co-existence of flexible PEEK backbones, flexible fluorinated ether side chains, ionic transporting sulfonate groups, and pent-dentate super ionic sulfonimide groups in the molecule structures.

## Introduction

Owing to their high power and energy densities, lithium ion batteries (LIBs) are considered as one of the most promising energy storage devices.[1] However, their applications in automotive power systems are still limited by their capacity and power density. Recently, silicon (Si) nano-particle based materials have attracted significant attention as high capacity active materials for lithium ion battery (LIB) anodes. Theoretically, its gravimetric capacity could approach approximately 10 times of that of conventional graphite.[2] However, during battery cycles, anodes containing Si particles tent to go through large volume expansion and contraction caused by Li$^+$ ion insertion and extraction generating mechanical stress and gaps or voids. On full lithiation to form the alloy of $Li_{4.4}Si$, Si particles could undergo drastic volume expansion of ~300%.[3, 4] It is observed that long time cycling under high current results in cracks in the anodes, pulverization of Si particles, loss of contact between the Si particles and its surrounding media, and excess growth of solid-electrolyte interphase (SEI),[5-8] leading to rapid decay in battery performance.

Recently, studies showed that the stability and irreversible capacity losses of the battery may also be affected by the binder's used in the anodes.[9, 10] For example, water soluble sodium carboxymethyl cellulose (CMC) binders performed better than poly(vinylidene) difluoride (PVDF) binders in silicon-based electrodes.[4, 11] Si based anodes prepared with CMC binder may be cycled at the high specific capacity of about 1100 mAh g$^{-1}$ for 70 cycles while similar anodes using PVDF binder showed no cycling capability.[12] The electrochemical performance of silicon based anodes can be further improved by using the binders extracted from brown algae or carboxymethyl chitosan.[9, 13] In the charging and discharging processes, lithium-ions need to be transferred at the interface between the electrodes and the electrolyte, as well as inside the active materials and porous spaces of the electrodes, therefore, the kinetics of these processes in part determine the overall battery performance. It seems that currently reported binders still lack the adequate functionality to tightly bind the silicon based active particles, adapt to the large volume fluctuation and facilitate the transportation of Li$^+$ ions under high rate charging/discharging.[14] Although stable cycling of the anodes could be achieved using these binders at lower rates, their electrochemical performance are still problematic under high rates.

Fluorinated polymers with sulfonimide groups were studied since the 1990s, especially by DesMarteau and Watanable et al.[15, 16] The lithiated forms of the fluorinated ionic polymers had low lithium dissociation energy due to the delocalization of the



**Scheme 1**. The molecular structural of (a) SPEEK-PSA-Li, (b) SPEEK-PSI-Li, (c) PSU-PSI-Li.

negative charge of the conjugated base over the functional groups stabilized by the electron withdrawing fluorinated sulfonyl chains.[17] Recently, lithiated fluorine containing ionomers have been developed as effective electrode binders to enhance the ionic conductivity and $Li^+$ ion diffusion in high rate cycling processes.[14, 18-20] We have also demonstrated that using lithiated sulfonated poly(ether-ether-ketone) containing fluorinated sulfonic acid side chains (SPEEK-PSA-Li) as binder could greatly enhance the electrochemical performance of lithium battery electrodes under high rates. To study the impact of binder with sulfonimide groups with higher ionic dissociation potential, two novel binders containing lithiated fluorinated sulfonimide groups (SPEEK-PSI-Li and PSU-PSI-Li) were prepared and investigated. In this paper, we want to know if the novel fluorine containing sulfonimide binders containing flexible fluorinated ether linkages could mitigate the negative impact caused by the drastic volume fluctuation from silicon nano-particles during high rate cycling in the high capacity anodes.

## Experimental

### Preparation of binder solutions and composite anodes.

The anodes comprised 60 wt. % of Si, 20 wt. % of Super P (Timcal Graphite & Carbon, Switzerland) and 20 wt. % of binder. Si powder with average particle sizes of 50 nm obtained from Jiechuang New Material Technology Co. (China). PVDF (HSV900, Arkema Co., LTD, France) in NMP, Na-CMC ($M_w$=500000 g/mol, Alfa Aesar, USA) and alginate ($M_w$=250000 g $mol^{-1}$, Aladdin) in water with the addition of ethanol (5 wt. %) were used as binders for the anodes. Lithiated ionomers, as shown in Scheme 1, such as SPEEK-PSI-Li, SPEEK-PSA-Li, PSU-PSI-Li (synthesis and characterization are in Supporting Information), dissolved in 1-methyl-2-pyrrolidone (NMP, AR, Aladdin, China) to form a 4 wt. % solution were used as binders. The lithiated ionomer membranes were prepared by solution casting method.

### Electrochemical and adhesion measurements.

Electrochemical properties of the anodes were tested in coin cell with a size of 20 mm. Working electrodes for cells were prepared by casting the slurry consisting of 60 wt. % of active material (Si nanoparticles), 20 wt. % of conductive Super P carbon, and 20 wt. % of the binder onto copper foil. The electrolyte consisted of a solution of 1M $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 v/v). Lithium foils were used as counter electrodes. The mass loading of the active material was about 1.2 mg $cm^{-2}$. These cells were assembled in an argon-filled glove-box and galvanostatically cycled between 0.01 V and 2.0 V on a battery tester (Land CT 2001 A). Their AC impedance was measured at an Autolab electrochemical workstation (CH Instruments) with the frequency range and voltage amplitude sets as 100 KHz to 0.01 Hz and 10mV, respectively.

The vertical peeling experiment was used to test the adhesion ability between the coating of the electrode and the Cu current collector on an omnipotent electronic stress-strain tester (UTM, Instron 567, USA). The silicon anode electrodes with different binders were prepared, and an adhesive tape with a 1 cm width was stick to the coating of the electrode. The Cu collector plane was horizontal fix to the lower chuck, and one side of the adhesive tape was nipped by the upper chuck. The tensile rate was 10 mm $S^{-1}$.

A specific weight-loss process was developed to assess the relative adhesion capability of the binders to hold the electrode materials together in electrolytes. The anodes were first immersed into the liquid electrolyte solutions for 1 week. After the excess liquid on the surface was removed with tissue paper, the anodes was then dried in an vacuum oven at 60 $^oC$ overnight and then placed ultra-sound for 60 min into a small glass bottle in the cell of ultrasonic wave cleaner (Branson CPX1800, USA). The weight loss of the electrodes as well as the visual appearance of the resulted electrode surfaces were recorded (average value of three times repeated) respectively.

Scanning electron microscopy (SEM) was performed using a Htachi S-4800 to detect the morphology of the electrodes, which was sputtered with gold for 100 sec beforehand.

## Results and discussion

### Charge-discharge performance.

To mitigate the negative impact from the drastic volume fluctuation of Si nano-particles during battery cycling, both the strength of ionic functional groups and the flexibility of the polymer backbone are important at the presence of flexible fluorinated ether side chains. Three ionomers, containing the flexible fluorinated ether side chains, SPEEK-PSA-Li (IEC=1.45 meq $g^{-1}$), SPEEK-PSI-Li (IEC=1.73 meq $g^{-1}$) and PSU-PSI-Li (IEC=1.02 meq $g^{-1}$) were prepared and tested as the binders for Si particle based battery anodes. The battery capacity retention after 10 cycles, as well as binder ionic conductivity and electrode vertical peeling strength, are

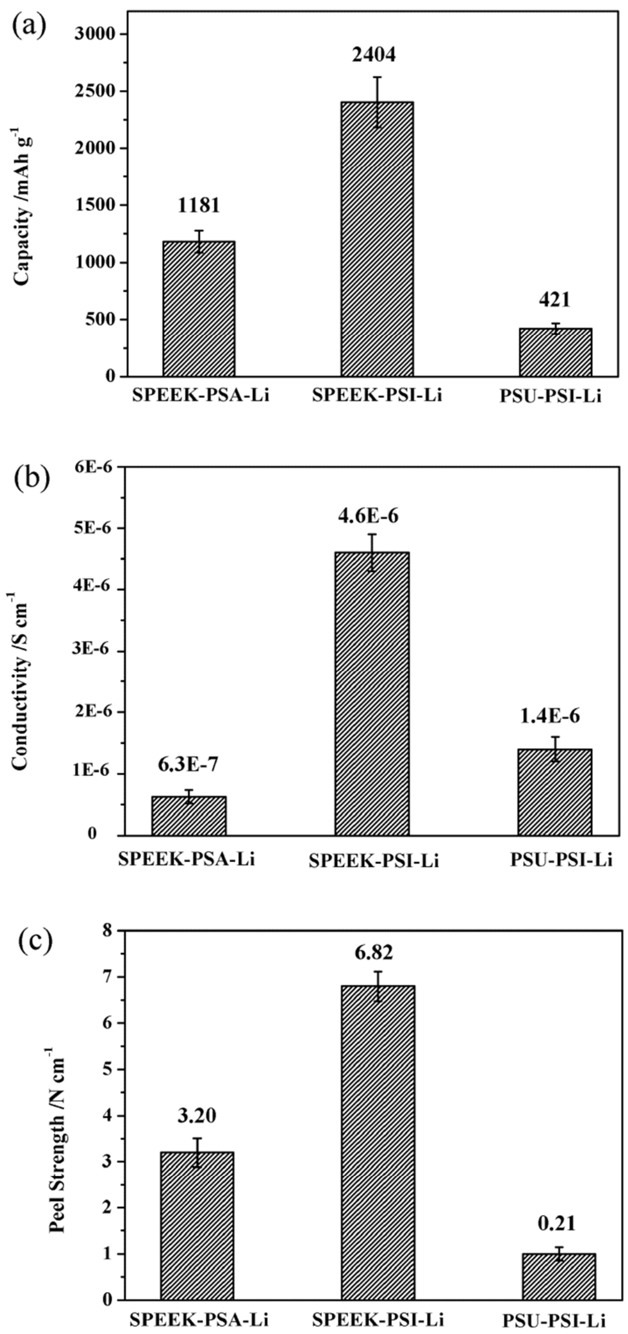


**Fig. 1** (a) Capacity retention of Si anode with SPEEK-PSA-Li, SPEEK-PSI-Li and PSU-PSI-Li binders at the rate of 400 mA g$^{-1}$ after 10 cycles. (b) Conductivity of SPEEK-PSA-Li, SPEEK-PSI-Li and PSU-PSI-Li membrane. (c) Vertical peeling strength of the electrodes with different binders.

compared in Fig. 1. SPEEK-PSI-Li showed the highest peeling strength (6.82 N cm$^{-1}$), capacity retention after 10 cycles (2404 mAh g$^{-1}$), as well as the highest ionic conductivity (4.6E-6 S cm$^{-1}$) with flexible polymer chains and stronger ionic groups. SPEEK-PSA-Li electrode showed less peeling strength (3.20 N cm$^{-1}$) and capacity retention after 10 cycles (1181 mAh g$^{-1}$) with weaker ionic groups. Electrodes with PSU-PSI-Li binders showed less peeling strength and capacity retention because of its rigid PSU backbone.

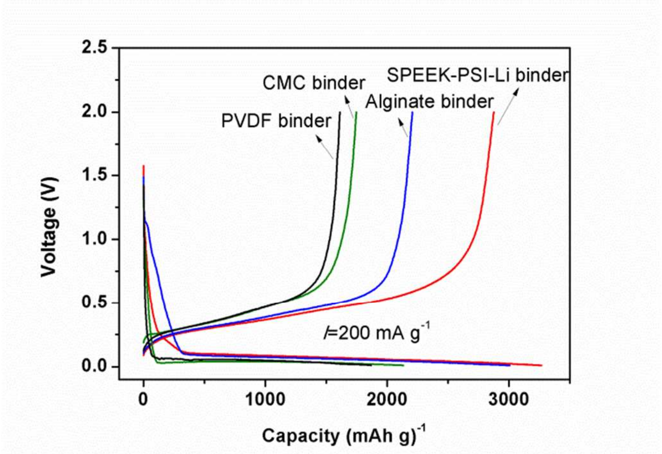


**Fig. 2** Comparison of first galvanostatic reduction and oxidation curves of Si anode with different binders.

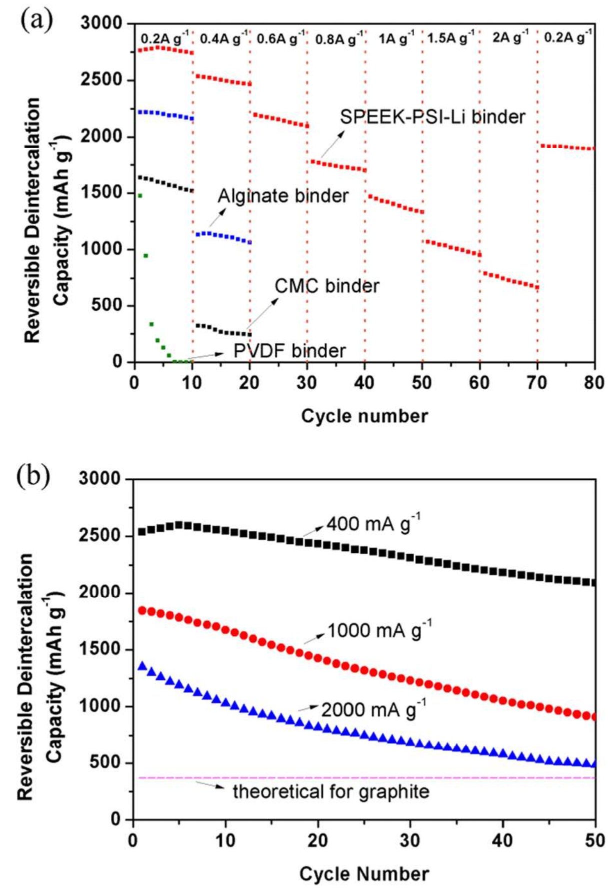


**Fig. 3** (a) Rate performance of Si anode with different binders recorded at 0.01V-2V; (b) the long cycling performance of Si anode with the SPEEK-PSI-Li binder at different rate.

As shown in Fig. 2, the electrochemical performance of SPEEK-PSI-Li binder was also superior to reported conventional binders in silicon based electrodes. All the anodes exhibit a long flat plateau at approximately 0.4 (vs. Li/Li$^{+}$) during the first charging (lithiation) voltage profiles of the Si anode at 200 mA g$^{-1}$. Si anodes with PVDF, CMC and alginate binders showed lower charge/discharge capacity of 1869/1612 mAh g$^{-1}$ (CE=86.2%), 2131/1746 mAh g$^{-1}$ (CE=81.9%),

**Table 1**. Weight lost percentage of the Si anode electrode with different binder after treated with ultrasound.

| | PVDF/mg | CMC/mg | Alginate/mg | SPEEK-PSI-Li/mg |
|---|---|---|---|---|
| original | 1.52 | 1.52 | 1.50 | 1.53 |
| after treated | 0.95 | 1.31 | 1.32 | 1.38 |
| weight loss percentage | 37.5 % | 13.8 % | 12.0 % | 9.8 % |

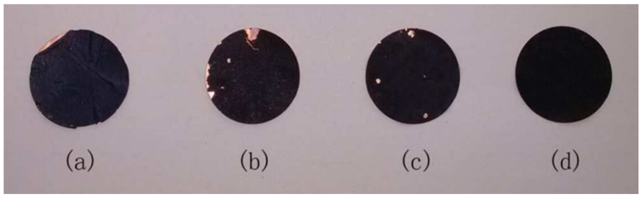


**Fig. 4** Visual appearance of anodes after ultrosonification with (a) PVDF (b) CMC (c) Alginate (d) SPEEK-PSI-Li binders.

3004/2207 mAh $g^{-1}$ (CE=73.5%). Si based anodes with SPEEK-PSI-Li binder demonstrated the best charge/discharge capacity of 3266/2874 mAh $g^{-1}$, with a highest initial Coulombic efficiency (CE) of 88.0%.

These results confirmed that the existence of binding ionic group and the adaptable backbone structures are important in mitigating the negative effects caused by the drastic volume change of Si particles. As shown in Fig. 3, the superiority of SPEEK-PSI-Li binder over traditional binders for Si-based anodes in lithium ion batteries can be further illustrated in the long term charging and discharging cycles under higher current rates. The poor performance of PVDF can be explained by its lack of ionic groups to bind to Si particle surface, leading the formation of gaps and voids after cycling, CMC binder showed improved performance by having ionic functional groups, –OH and $–CO_2^-$, to bind to the oxidized Si particle surfaces. The performance of alginate binders was further enhanced by having flexibility in the sugar backbones in addition to the ionic binding groups.[9]

The poor high rate performance of the cell with CMC and alginate binder is partially due to the lack of strong ionic functionality to facilitate rapid cation transportation, resulting in salt concentration polarization and salt depletion within the electrodes during high rate charging and discharging.[14] In the case of using SPEEK-PSI-Li as anode binder, the conformation of not only PEEK back bones but also the side fluorinated ether chains could be changed to accommodate the volume change. The introduction of fluorinated ether portion not only reduced the solubility of the material in the electrolyte, but also enhanced the Li ion dissociation degree from the anions. The pent-dentate sulfonimide ionic not only provide high capability to bind to the Si particle surface via hydrogen or Li ionic bridges, but also can associate with sulfonate groups from the flexible SPEEK back bones to form high efficient cation transporting nano-channels to allow rapid lithiation and de-lithiation during the battery cycling as illustrated in Fig. 8. As shown in Fig. 3, even at a high current rate of 2000 mA $g^{-1}$, the capacity of the anode was kept above 500 mAh $g^{-1}$, which could quickly return to about 2000 mAh $g^{-1}$ when the current was changed back to 200 mA $g^{-1}$.

Using the novel SPEEK-PSI-Li binder, a high capacity Si based anode with long term cycling stability can be developed for lithium ion battery running at high current rate. Fig. 3(b) displays the long term cycling performance of Si/SPEEK-PSI-Li anodes for 50 cycles at different rates. The discharge capacity have a slight increase during the first few cycles for a current rate of 400 mA $g^{-1}$, probably due to the cell formation in the initial cycles, in which the active material Si were thoroughly wetted by the liquid electrolyte solution. The retention capacity of this rate was still 2090 mAh $g^{-1}$. Even when the cycling current rate was increased to 2000 mA $g^{-1}$, the specific capacity was retained at about 510 mAh $g^{-1}$ after 50 cycles, still much higher than the theoretical capacity of graphite.

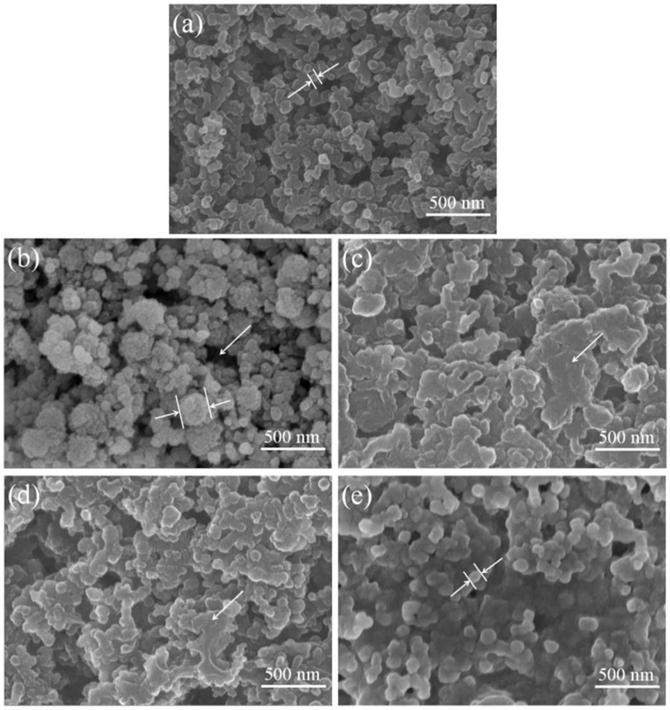


**Fig. 5** SEM images of (a) Si nano-particles electrode before cycling, and (b-e) Si anode with PVDF, CMC, alginate and SPEEK-PSI-Li as binder respectively after 50 cycles.

### Adhesion performance.

The superior performance of SPEEK-PSI-Li binders can further be illustrated in the specific weight loss procedure as described in the experimental. As shown in Table 1 and in Fig. 4. PVDF provided the worst adhesion for the particles in the electrodes, with the highest weight loss of 37.5% with no ionic binding groups, while CMC and alginate show better adhesive capability with less weight loss of 12-14%. The adhesion capability of SPEEK-PSI-Li was the best with the least weight loss of less than 10%.

It should be also noted that the solubility of binder in electrolyte could affect the binding strength.[9] The fluorinated section in the SPEEK-PSI-Li polymer chains could provide non-swellable fluorinated barrier sections in the binding regions to enhance the binding strength. The interaction between the binder and Cu foil are also very important. SPEEK-PSI-Li provides good adhesion between the electrode materials and the

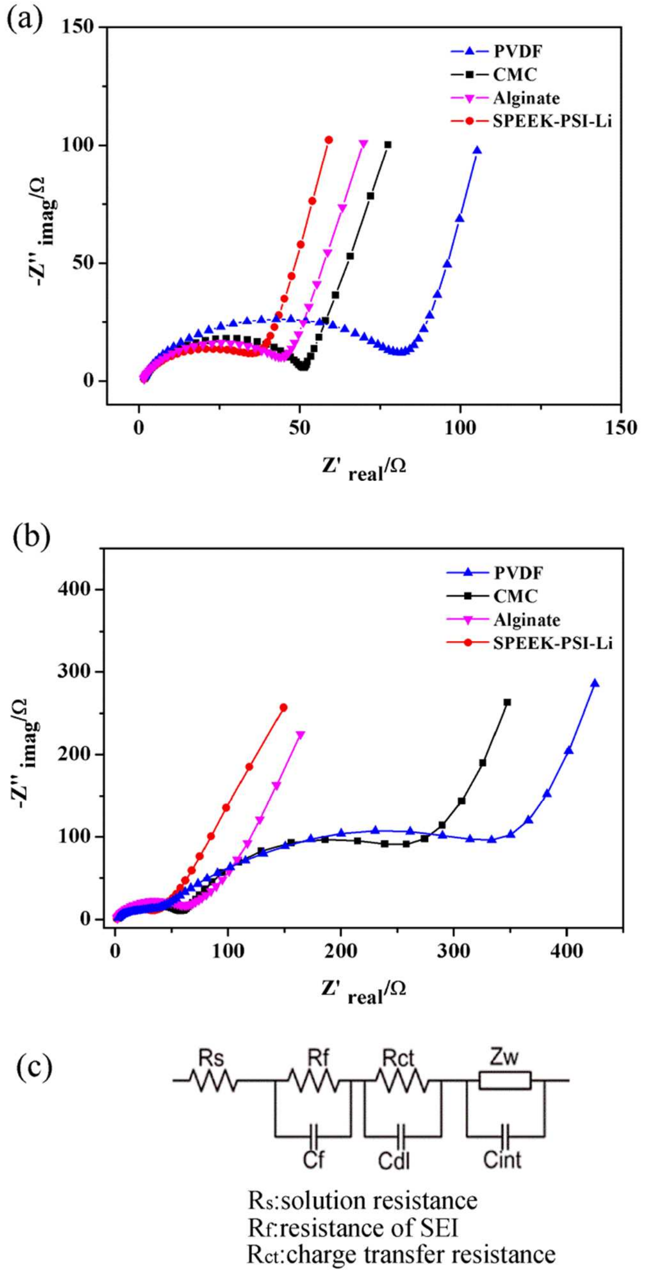


**Fig. 6** Nyquist plots of anode with different binders; (a) after 2 cycle, (b) after 50 cycle, (c) The equivalent circuit for the fitting of the experimental electrochemical impedance spectra of lithium ion intercalation or de-intercalation.

Cu current collector and no Cu foil surface was exposed. On the other hand, the images of Si/PVDF, Si/CMC and Si/alginate all exposed a portion of bare Cu foil on its top surface after the ultrasound treatment resulting from weak adhesion to the Cu surfaces.

SPEEK-PSI-Li binder could stick to the surfaces of Si nano-particles and flexibly adjust with the size and shape change of Si nano-particles during lithiation and de-lithiation to prevent the destruction of electrical and ionic transporting network. As shown in Fig. 5, Si nano-particles of spherical shape with 50-100 nm in size were effectively bound together in the beginning. After cycling, voids and cracks were formed in Si/PVDF electrode (Fig. 5(b)), where the Si particles aggregated to non-connected big chunks with no adhesion. The Si nano-particles lost most of their shapes and merged into the blocks of SEI materials in the electrodes of Si/CMC and Si/alginate, resulting in the loss of reactive contact areas to the electrolyte. It is clear that Si nano-particles in Si/SPEEK-PSI-Li (Fig. 5 (e)) still preserved their size and shapes after cycling to a large extent.

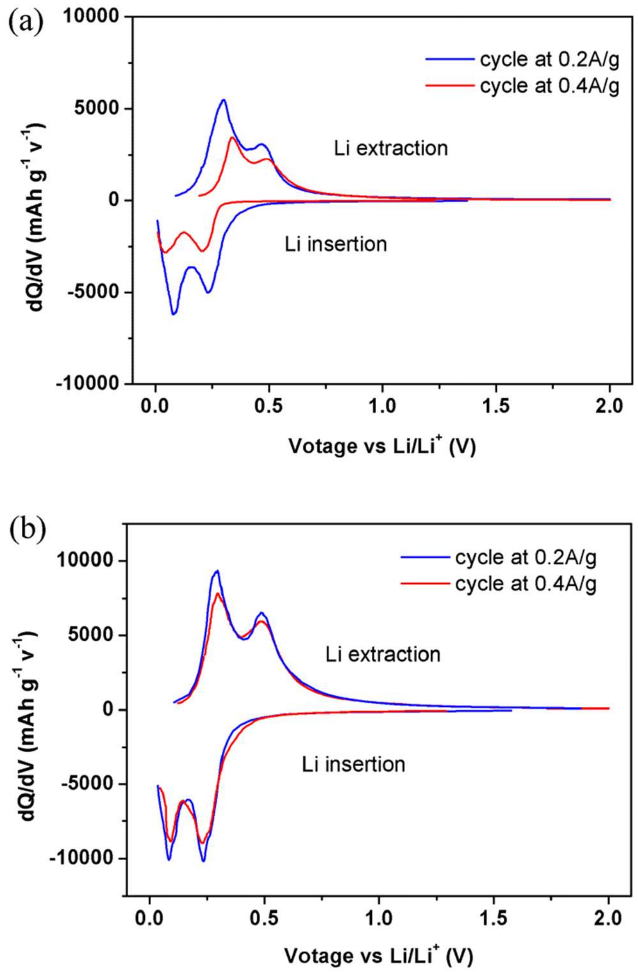


**Fig. 7** Differential capacity dQ/dV curve of the second cycles of the as-prepared Si anode with (a) Alginate binder and (b) SPEEK-PSI-Li binder

### Electrochemical impedance spectroscopy (EIS) performance.

Fig. 6 shows the Nyquist plots of Si anode with different binders after 2nd and 50th cycle. After the 2nd (Fig. 6(a)) cycles, all the Nyquist plots were composed of a large semicircle from the high to medium frequencies and a nearly straight line at low frequencies. The semicircle at high to medium frequencies is generally accepted as the migration of lithium ion in the surface layer while the low frequency straight line is likely the result of lithium ions diffusion through the electrodes.[21] Generally, good interaction between the Si and the binder make it easier to form a relative more uniform coverage of SEI layer on the Si surface. As observed in the SEM images, after cycling, the network of the binder surrounding the nano-particles may degrade to some extent, which would lead to increase in resistance. As shown in Fig. 6(b), no additional semicircle was observed in the case of Si/SPEEK-PSI-Li and Si/alginate. While the Si/PVDF and

**Table 2**. Resistance values obtained from fitting impedance spectra

| | After 2 cycle | | | After 50 cycle | | |
|---|---|---|---|---|---|---|
| Binder Type | $R_s/\Omega cm^{-2}$ | $R_f/\Omega cm^{-2}$ | $R_{ct}/\Omega cm^{-2}$ | $R_s'/\Omega cm^{-2}$ | $R_f'/\Omega cm^{-2}$ | $R_{ct}'/\Omega cm^{-2}$ |
| PVDF | 1.3 | 21 | 62 | 1.3 | 32 | 362 |
| CMC | 1.2 | 14 | 37 | 1.2 | 59 | 228 |
| Alginate | 1.3 | 12 | 33 | 1.4 | 27 | 50 |
| SPEEK-PSI-Li | 1.3 | 11 | 25 | 1.3 | 14 | 30 |

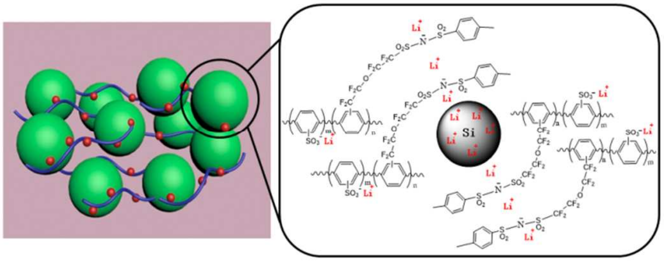


**Fig. 8** Illustration of the interaction between SPEEK-PSI-Li and Si nano-particles.

Si/CMC electrodes showed two additional semicircles at the high and middle frequency region after 50th cycles, corresponding to the formation of thick SEI layers and increase in charge transfer resistances.

The impedance data were fitted into equivalent electrical circle analysis using Z-simpwin software as shown in Table 2, after 50 cycles, the charge transfer resistance $R_{ct}$ for the electrodes made with a SPEEK-PSI-Li was about 20%. While the change of $R_{ct}$ in the case of PVDF and CMC binders increased by 500% from the 2nd cycles, the change of $R_{ct}$ for the electrodes made with Si/alginate anodes performed slightly better than CMC due to its increased in chain flexibility. Si/SPEEK-PSI-Li anodes showed the lowest interaction resistance due to its higher lithium ion conductivity, packing flexibility, and other preferred characters from the structures as discussed before.

### Polarization performance.

The superiority in cycling performance of SPEEK-PSI-Li can be further illustrated in the dQ/dV profile of Si anode in Fig. 7 under two current rates of 200 mA $g^{-1}$ and 400 mA $g^{-1}$. At 200 mA $g^{-1}$, the lithiation peak at 0.08 V corresponding to the long flat plateau in the discharge voltage profile, related to the phase transition of crystalline Si to amorphous lithium silicide, while the lithiation peak around 0.25 V come from the phase transition between amorphous $Li_xSi$ phases; the de-lithiation peaks at 0.31 V and 0.50 V related to the extraction of Li from Si particles,[13] corresponding to the initial slope in the charge voltage profile. When the current rate was increased to 400 mA $g^{-1}$, the Li insertion and extraction voltage profile of the anode with alginate binder showed an obvious shifting in peak positions and lowering in capacity due to the polarization. It is interesting that the Li insertion and extraction profiles of the anode with SPEEK-PSI-Li binder exhibit no obvious shift and much less capacity change, showing no obvious increase in over-polarization loss at this rate. Efficient intrinsic ionic transporting channels may have been established in the case of SPEEK-PSI-Li and eliminated over-polarization. As shown in Fig. 8, the flexible SPEEK-PSI-Li polymers physically twist around the Si nano-particles to allow the effective binding of sulfonimide functional groups to the cations on the surfaces of the nano-particles, while the association of the sulfonimide and sulfonate functional groups in the structures to form ionic domains with effective $Li^+$ cation transportation channels. The association of fluorinated ether linkage formed non-soluble fluorinated domains to prevent electrolyte etching. More importantly, the size and shape of these components may be adjusted to mitigate the negative impact caused by the drastic volume fluctuation from Si nano-particles via adjustment in the flexible PEEK backbones or the fluorinated ether side chains.

## Conclusions

In summary, the negative impact caused by the large volume change from the Si nano-particles in lithium ion battery anodes during high rate cycling can be mitigated by using novel fluorine containing ionic binders with sulfonimide groups and structural flexibility. When cycled under high rates, the discharge capacity of comparison binders such as PVDF, CMC, alginate, SPEEK-PSA-Li and PSU-PSI-Li faded quickly, but the Si anode with SPEEK-PSI-Li showed a superior cycling stability, which could be attributed to its high cohesion capability, low solubility in electrolyte, high adaptability to volume fluctuation and high ionic conducting capability resulting from the co-existence of flexible PEEK backbones, flexible fluorinated ether side chains, ionic transporting sulfonate groups, and pent-dentate super ionic sulfonimide groups in the structure. It can be seen that the use of SPEEK-PSI-Li binder offer an attractive way to stabilize of the performance of Si based anodes under high rate cycling, bearing high potential for applications in high performance lithium ion batteries.

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## Notes and references

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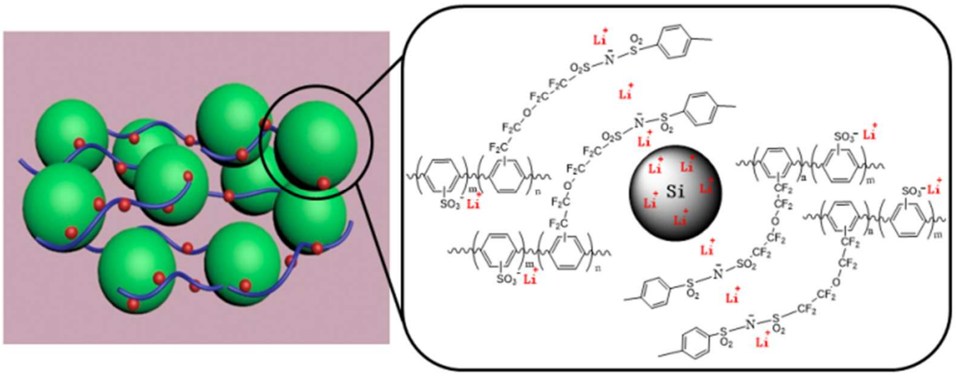

Sulfonated polyether ether ketones, bearing pendant lithiated fluorinated sulfonimide groups (SPEEK-PSI-Li) used as novel ionic binders not only provide good adhesion property, but also effectively reduce the over-potential during rapid charge and discharge cycles which lead to a better capacity retention for Si based anode Lithium-Ion Battery.