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Cycling performance of SiO_x-Si-C composite anode with different blend ratios of PAA-CMC as binder for lithium sulfur batteries

Swamickan Sathya¹ · Charlin Soosaimanickam¹ · Federico Bella² · Dong Jin Yoo³ · A. Manuel Stephan¹

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Abstract

Silicon (Si) -based materials have been identified as a potential alternative anode owing to their superior theoretical capacity compared to conventional graphitic carbon. Nevertheless, the huge volume change (approximately 300%) that occurs while cycling still hampers this system from 100% practical applications. Silicon-monoxide (SiO_x)-based anode materials, on the other hand, are being explored extensively due to their unique properties such as high theoretical capacity, formation of Li₂O and LiSiO₄ during initial lithiation process that act as a natural volume buffer matrix to accommodate volume changes and formation of a stable solid electrolyte interphase layer, which improves the cyclability and capacity retention. Although poly (vinylidene fluoride) (PVdF) is widely used as a binder, the weak van der Waals forces between PVdF and silicon-based particles fail to bind particles effectively, when substantial volume change occurs. Herein, we prepare a series of SiO_x-Si-C electrodes with different binders poly (acrylic acid) (PAA), carboxyl methyl cellulose (CMC) and their blends as binder. The prepared polymeric blends are subjected to thermal, morphological, mechanical and physico-chemical analyses. The Li/SiO_x-Si-C cell assembled with 100% PAA as binder delivered a discharge capacity of 1908 mAh g⁻¹ on its first cycle and 724 mAh g⁻¹ on its 100th cycle with a fade in capacity of 11.8 mAh g⁻¹ per cycle. Upon the incorporation of CMC in the PAA blend the cycling performance was found to be poor. Among the various investigated compositions, the electrode with sole poly (acrylic acid) as a binder offers the highest discharge capacity and this is attributed to the high concentration of the functional (carboxylic) group which forms strong hydrogen bonds with -OH groups on the SiO_x or carbon surface. The interfacial properties of the polymeric binders are thoroughly investigated by spectroscopies and electrochemical tests.

Keywords Silicon anode · Polymeric binders · Poly (acrylic acid) · Electrochemical impedance spectroscopy · Lithium-Sulfur batteries

Introduction

Though the switching of internal combustion engine to hybrid electric vehicles, and the reduction of greenhouse gas emissions can be facilitated by lithium-ion batteries, the

limited energy and power densities impede these systems from achieving 100% utilization [1–3]. Numerous attempts have been made to address this challenge by developing novel electrode and electrolyte materials. Recently, silicon sub-oxides (SiO_x, 0 < x < 2) are projected as potential anode materials owing to their abundance on earth's crust, ability to operate at lower potentials, low cost, facile synthesis methods, and environmental friendliness. Additionally, these materials offer a high theoretical capacity of 2615 mAh g⁻¹ and enhanced cycling capability than silicon with smaller volume change (~160%) while cycling. Despite these advantages the formation of Li₂O and LiSiO₄ during the initial lithiation process is due to the reaction of lithium ions with SiO_x, which decreases the specific capacity. Nevertheless, the formed Li₂O and LiSiO₄ act as buffer matrices and accommodate volume changes, which promotes the cyclability and capacity retention. Though the formation of Li₂O

✉ A. Manuel Stephan
amstephan@cecni.res.in

¹ Electrochemical Power Sources Division, CSIR- Central Electrochemical Research Institute, Karaikudi 630003, India

² Department of Applied Science and Technology, Politecnico di Torino, 10129 Torino, Italy

³ Department of Life Science, Department of Energy Storage/Conversion Engineering of Graduate School (BK21 FOUR), Hydrogen and Fuel Cell Research Center, Jeonbuk National University, 567 Baekje-daero, Jeonju 54896, Republic of Korea

and LiSiO_4 is advantageous to prevent pulverization of SiO_x complexes, several critical issues, such as inadequate rate capability, low Coulombic efficiency, and an extremely short cycling life at elevated current rates occur due to the low electrical conductivity ($6.7 \times 10^{-4} \text{ S cm}^{-1}$), and poor lithium ion diffusion and are to be resolved. To alleviate these issues, combining SiO_x with conductive layers of carbon or carbon matrix provides high conductivity and can significantly improve the charge transfer capability. In our earlier report, a series of electrodes were prepared based on SiO_x -Si-C of different compositions. Silicon nanoparticles could accommodate the huge volume change that occurs during lithium alloying and de-alloying processes. The polymeric binders play a key role in the electrodes of energy-storage devices; however, less attention has been paid to increase their performances and the available reports are very scanty. In general, polymeric binders hold critical components of batteries such as electrode active material, conductive carbon, solid additives and current collector, while charge/discharge process is going. The binder plays a significant role in dispersing critical components homogeneously, provides mechanical integrity by holding the particles together with a current collector through mechanical, intermolecular, or chemical forces in addition to electronic contact [4]. The ultrahigh capacity active materials experience large volume change during cycling and tend to generate higher stress than graphite and leads for delamination from the electrode surface. The most commonly used poly(vinylidene fluoride) PVdF, a linear type-homopolymeric binder though possesses higher binding capability, good electrochemical stability and better wettability (useful to transport lithium ions to the active material surface) for transporting lithium ions to the active material surface. However, the weak van der Waals force between PVdF and active material particles usually fail to bind particles together strongly during substantial electrode volume changes, specifically when silicon-based materials are used [5]. Polymeric materials such as linear, branched, cross-linked and self-healing polymers have also been extensively studied [6]. In general, the hydrogen bond plays a vital role in strengthening the adhesive force of a polymeric binder [7, 8]. The structures of binders greatly affect the silicon-based anodes through multiple interactions, such as chemical bonding, conjugate conductivity, mechanical interlocking, van der Waals forces, and electrostatic forces, which are mainly determined by the backbone structures and functional groups of polymeric binders [8, 9]. Recently, the importance, properties and applications of binders for different electrode materials have been extensively reviewed by several researchers [10–12]. For example, sodium alginate binder assists in building a stable solid-electrolyte interphase (SEI), but the hydroxyl groups that remain after vacuum annealing at 105°C represent an issue since they react with PF_5 produced from LiPF_6 salt at elevated temperatures. The

resulting phosphorous oxyfluoride (OPF_3) can lead to the decomposition of carbonate solvents, which, in turn, cause rapid degradation of the Si anodes and increased cell impedance [9, 13]. In general, PVdF is known to provide a stable cycling performance for the electrode with active materials that do not undergo volume changes (or negligible volume change). On the contrary, in the case of electrode with silicon as active material the PVdF's weak resistance to deformation is incapable of keeping silicon particles upon deformation. This in turn leads to poor contact among the silicon particles in the subsequent cycles.

Carboxymethyl cellulose (CMC), a water-soluble substance, has been extensively studied as an inexpensive and natural binder [14]. According to Chen's group, [15, 16] binder selection is crucial, especially when alloy anodes are used. Dahn et al. [17] extensively studied the binding properties of CMC with silicon-based anode materials, and it emerged that brittle binders are able to endure the extreme volume changes. Additionally, CMC alters the surface chemistry of silicon particles and reduces the capacity loss of the cell.

On the other hand, polyacrylic acid (PAA) exhibits a strong adhesion property through its hydrogen bonding interaction between the carboxyl ($-\text{COOH}$) groups in PAA with the hydroxyl group ($-\text{OH}$) of carbonaceous materials and aluminum substrate current collector [18]. Cho and co-workers [19] employed a three dimensionally cross-linked PAA and CMC condensation reaction (dehydration) in which PAA effectively formed a cross-linked structure through the condensation reaction with CMC. The resultant binder was used to evaluate the performance of SiO_2 anode material for lithium-ion batteries (LIBs). Huang et al. [20] prepared a SiO_x composite electrode using three different types of binders: (PVdF), (PAA), and LA132 (a copolymer with a major chain of polyacrylonitrile; the electrochemical performances were systematically investigated for the applications in LIBs. Numerous reports are available on the electrochemical and cycling performances of Si/ SiO_x -based electrode materials with different binders such as PAA, CMC and functionalities for the applications in LIBs. Instead, to the best of our knowledge no reports are available on the role of polymeric binders for Si/ SiO_x -based electrode materials for lithium sulfur (Li-S) batteries. Among the various compositions examined, the electrode composed with a ratio of SiO_x -Si-C at 70:12.5:12.5 was found to be optimal in terms of discharge capacity with lithium half-cell configuration. Therefore, in the present study a series of SiO_x -Si-C-based electrodes with PAA: CMC binders bearing with different ratios (100:0, 60:40, 50:50, 25:75, 10:90, and 0:100) have been prepared and were subsequently tested and characterized in terms of charge-discharge and interfacial properties.

Experimental procedure

Materials

Poly (acrylic acid) ($M_w \sim 4,000,000$, Sigma-Aldrich) and sodium carboxymethyl cellulose (TCI, Japan) were used as received without further purification. The battery grade non-aqueous liquid electrolyte containing LiTFSI 1 M, 1,3 dioxolane and tetraethylene glycol dimethyl ether (Spectrochem) in a 1:1 (v/v) ratio, and 5% of fluoroethylene carbonate as an additive. Silicon suboxide SiO_x with a particle size of $5 \mu\text{m}$ (Osaka Titanium Corporation, Japan), silicon with particle size of $\leq 10 \text{ nm}$ were used as received. Graphitic carbon was used as a conducting carbon source.

Preparation and electrochemical characterization of the electrodes

The blends of polymeric binders for different ratios of PAA and CMC as shown in Table 1; both polymers were mixed by a kneading machine and subsequently hot pressed in order to ensure homogeneity. For characterization purposes, membranes containing 100% PAA, 50% PAA:50% CMC, 25% PAA:75% CMC and 100% CMC were used. SiO_x , silicon, carbon and the binder (PAA, CMC or PAA and CMC blends) were mixed with a ratio of 70:12.5:12.5:5 and the resulting slurries were subsequently prepared with water as a solvent as this composition was found to be optimal in terms of high discharge capacity in our earlier study on Li-S batteries [20, 21]. The slurry was spread on a copper current collector and dried in the air at room temperature for 6 h. The electrodes were punched into 14 mm diameter disks and dried in a vacuum oven at $110 \text{ }^\circ\text{C}$ overnight. The thickness of the electrode laminates was $\sim 15 \mu\text{m}$ and the total mass loading was $\sim 2.20 \text{ mg cm}^{-2}$. Finally, 2032-coin cells were assembled in an argon filled glove box comprising SiO_x -Si-C as working electrode, a lithium foil as counter electrode, the electrolyte ($100 \mu\text{L}$), and a separator (Celgard 2320).

Table 1 The composition of polymeric blends of PAA: CMC and their ionic conductivity data

Sample	PAA (%)	CMC (%)	Ionic conductivity ($\times 10^{-5} \text{ S cm}^{-1}$)
a	100	0.0	8.6
b	60	40	8.2
c	50	50	8.0
d	25	75	6.8
e	10	90	5.4
f	0.0	100	4.8

The thermal stability of the polymeric membranes was determined by a thermogravimetric analyzer (TGA) in the temperature range from 30 to $700 \text{ }^\circ\text{C}$. The mechanical properties of the polymeric membranes were characterized using a tensile analyzer (Tinius Olsen, H5KT) with a cross-head speed of 10 mm min^{-1} . Fourier transform infrared spectroscopy (FTIR) was carried out with a Bruker Optik GmbH, equipment to recognize the functional groups present in the polymeric binders. With the aim of investigating the swelling property of polymeric binders in the electrolyte the following equation was used to calculate the electrolyte uptake:

$$\text{Uptake} = \frac{W_w - W_d}{W_d} \times 100 \quad (1)$$

where, W_w and W_d are the weight values of the wet and dry samples, respectively. Electrochemical impedance spectroscopy (EIS) was performed using a VSP3 Biologic (France) workstation over a frequency range of 1 MHz to 100 mHz . The assembled cells were cycled between 0.005 and 2.5 V at a rate of $C/10$ using an Arbin BT2000 battery cycler at $25 \text{ }^\circ\text{C}$. The rate was calculated on the basis of the theoretical capacity of silicon, SiO_x and carbon. The de-lithiated electrodes were extracted from cycled cells and were very carefully washed with 1,3 dioxolane twice in order to remove residue of the electrolyte: then, they were dried and stored in a glove box for *ex-situ* analyses. The change in surface morphology of electrodes before and after cycling were examined by field emission scanning electron microscopy (FESEM, SUPRA 55VP, Germany) with an equipment working at an accelerating voltage of 5 kV . X-ray photoelectron spectroscopy (XPS, Thermo Scientific, USA) was carried out using an Al-K α X-ray radiation source (photon energy 1486.7 eV). The electrodes were transferred from the glove-box using a sealed transfer apparatus without exposure to air and the binding energy was corrected based on the C 1s of hydrocarbon at 284.2 eV .

Results and discussion

In order to determine the thermal stability of PAA, CMC and their blends thermo gravimetric analysis was performed in an N_2 -atmosphere. The TG traces of PAA, CMC and their blends are shown in Fig. 1. Regardless the type of polymer, the observed weight loss below $100 \text{ }^\circ\text{C}$ is attributed to the removal of moisture absorbed at the time of loading the samples. An irreversible weight loss starts at around $218 \text{ }^\circ\text{C}$ for pure PAA while for pure CMC it occurs at $250 \text{ }^\circ\text{C}$. When CMC is blended with PAA, the irreversible decomposition occurs at $233 \text{ }^\circ\text{C}$. Upon addition of CMC in the PAA matrix the thermal stability of the blend is increased that means higher than that of pure PAA. Typically, the removal of volatile products often happens from the side groups (e.g., OH

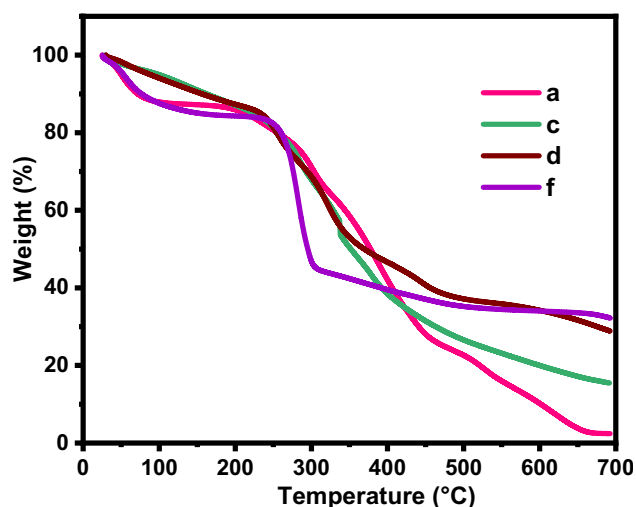


Fig. 1 TG-traces of samples a, c, d and f

groups) approximately below 260 °C [22, 23]. The second degradation can be ascribed to the chemical degradation from C-C bond scission [22]. For the PAA-CMC blends, the TG curves are split into two distinct peaks, one close to PAA and another one is close to PAA, which is a characteristic feature of immiscible polymers.

The surface morphology of PAA, CMC and their blends are depicted in Fig. SI-1. The pure PAA membrane shows a rough morphology with wrinkles while 100% CMC exhibits a relatively smooth morphology. Upon addition of CMC in the PAA matrix, the surface morphology becomes very smooth.

Figure 2 shows the FT-IR spectra of PAA, CMC and PAA-CMC blend polymeric membranes of different compositions. The peak (Fig. 2a) that appears at 1714 cm^{-1} represents the -C=O stretching band of -COOH in PAA due to the ester groups -(COO) . The peaks at 1451 and 1406 cm^{-1} represent the asymmetric and symmetric stretching vibration of the PAA carboxylate (COO^-) group. Similarly for the CMC samples the appearance of peak at 1603, 1422 and 1058 cm^{-1} are due to stretching vibration of C=C bonds, bending modes in alkane chains, and C-O stretching respectively. Apparently, upon blending PAA and CMC, the intensity of the peaks is significantly altered which indicates the interaction between the PAA and CMC [24, 25]. The reduction in the intensity and shift in the peaks are attributed to the absorption of free carboxylic acid groups are weakened and the carboxylic groups react with CMC [26]. The XRD patterns of the samples a, c, d and f are depicted in Fig. SI-2. Apparently both PAA and CMC show semi-crystalline nature and the crystallinity of CMC is reduced upon blending with PAA. The EDS data is also presented as Fig. SI-3 which represents the presence of their corresponding atoms.

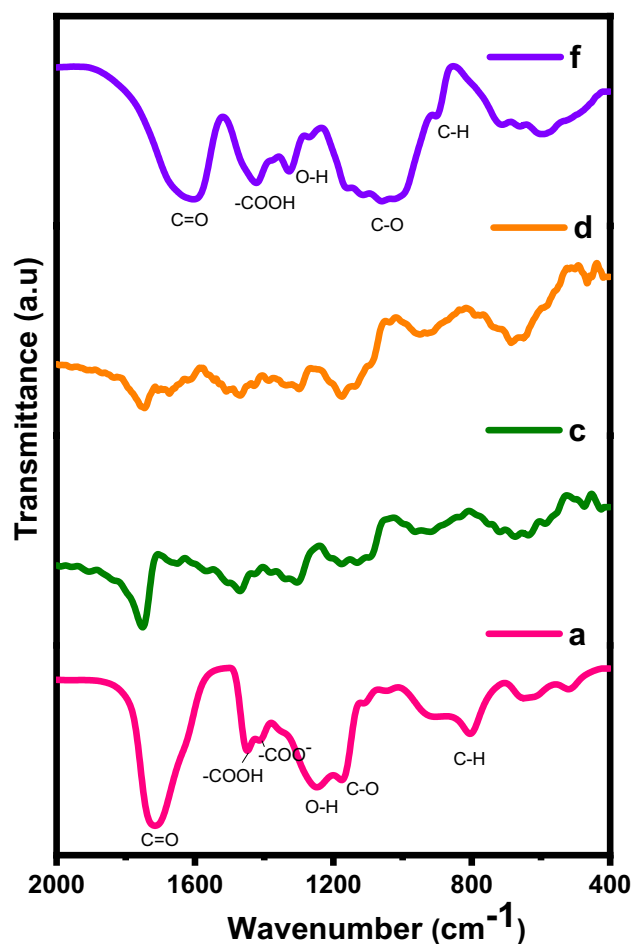


Fig. 2 FTIR spectra of PAA, CMC and their blends

The swelling property of polymeric binders in the electrolyte plays a key role in the electrochemical performance of batteries. The bond strength of the binder is reduced when the swelling nature of the polymeric material is high causing the anode materials to get de-laminated from the current collector, which deteriorates the integrity of the electrode structure and increases the contact resistance and subsequently the cycling performances.

The swelling test was performed by keeping the membrane in a non-aqueous electrolyte used for charge/discharge studies for the period of one week and their digital photographs are displayed in Fig. SI-4. It is quite obvious from the photographs that the membranes show a poorer swelling property with respect to PVdF, as reported by others [27].

The uptake of electrolyte as a function of time for different blend was calculated by Eq. 1. with the data shown in Fig. SI-5. The pure PAA binder showed inferior electrolyte uptake with respect to the CMC counter-part membrane and was attributed to the hydrophilic nature of the CMC.

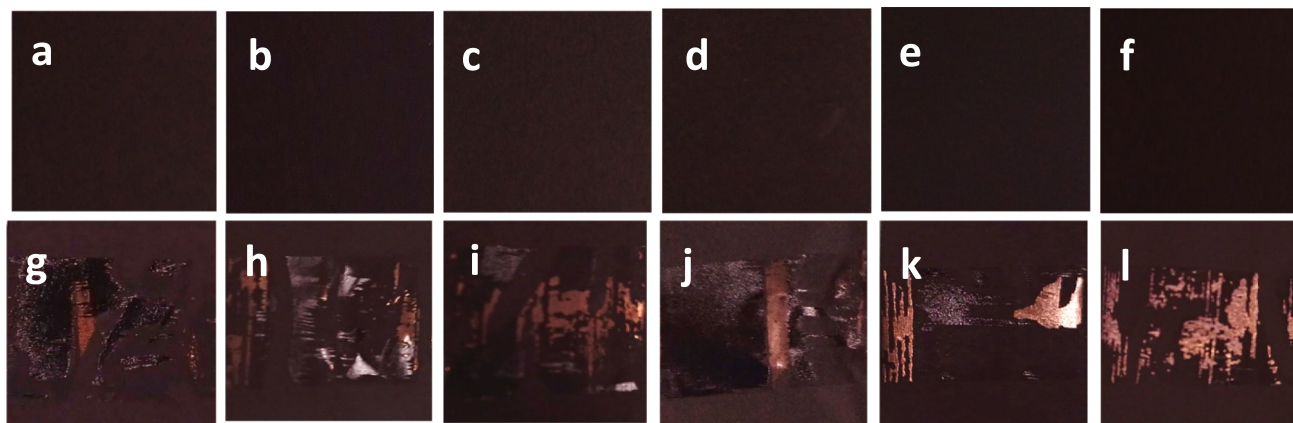


Fig. 3 Digital photographs of SiO_x-Si-C coated electrodes with different polymeric binders before coating (a–f using the legend shown in Table 1) and (g–l, below) after the peel-off test

The digital photographs of SiO_x-Si-C electrodes prepared with different binders before and after the peel-off test are shown in Fig. 3. The surface of the electrode coated with pure PAA exhibited superior gluing properties compared to electrodes coated with other polymeric binders. This improvement can be attributed to the strong adhesion facilitated by hydrogen bonding interaction between the carboxyl groups in PAA and the hydroxyl group of silicon particles and current collector [18].

Cyclic voltammetry

The cell, with pure PAA as a binder exhibited two oxidation peaks at 0.32 and 0.47 V in the 3rd, 4th and 5th cycles (Fig. 4a). During the de-lithiation process from the Si-Li alloy to silicon, the binder played a crucial role to maintain the internal resistances and SEI stability. Nevertheless, when the CMC was introduced in the PAA matrix the two oxidation peaks changed from their peak position and intensities

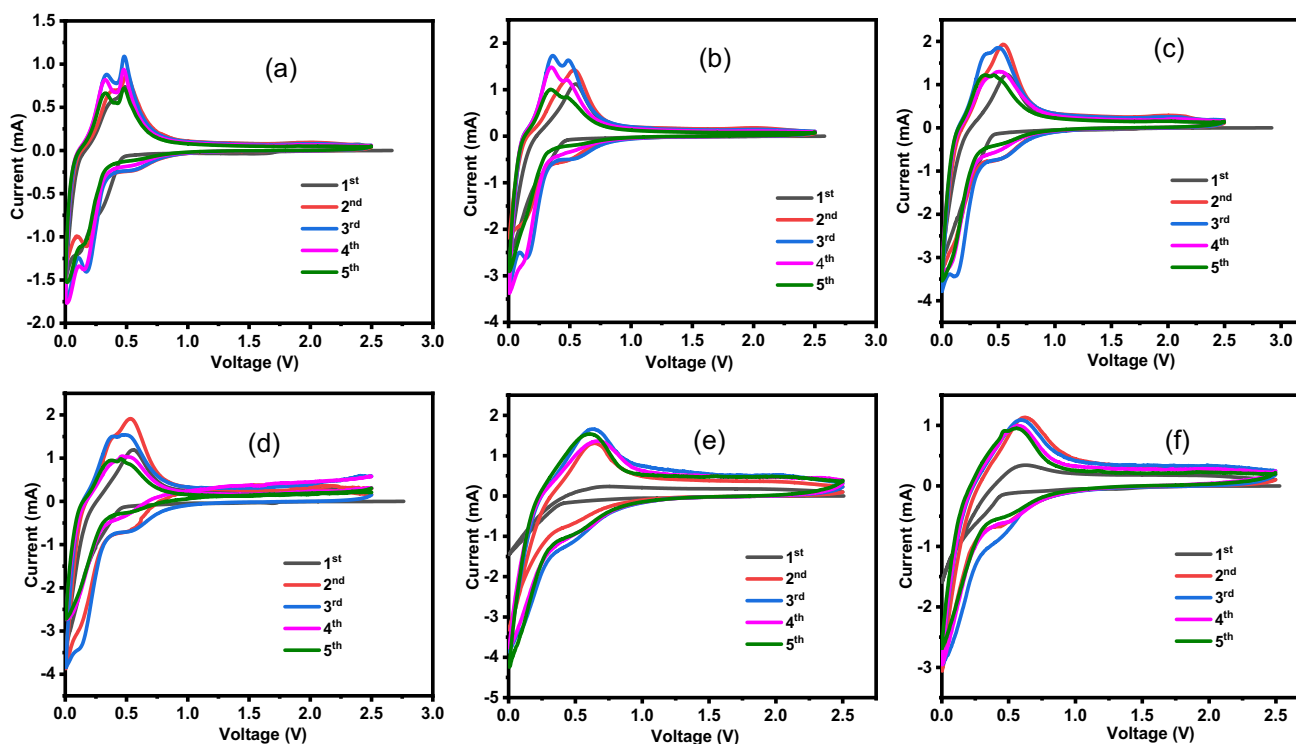


Fig. 4 Cyclic voltammograms of Li/SiO_x-Si-C cells assembled with electrodes having different binders (please refer to the legend shown in Table 1. The test was carried out at 0.1 mV s⁻¹)

upon cycling (Fig. 4b–f). This can be attributed to the delithiation process from the Si-Li alloy to silicon, since the binder loses the connection and delaminations from the current collector occurs, thus, making it difficult for the electron to be transported on the alloy surfaces. Instead, the pure PAA binder has been much stronger, alleviating the delamination from the current collector.

In the present study, the CMC-added blends and pure CMC binders also suffer from poor mechanical properties as evidenced from the tensile measurements (Fig. SI-6). Indeed, the tensile strength of the polymeric membranes is reduced when the content of CMC is increased which clearly demonstrates that PAA-based samples are stronger than the CMC counterpart, and the PAA-CMC blends provides mechanical integrity during volume expansion. Moreover, the presence of the carboxyl groups in PAA play a vital role to alleviate the volume expansion of the SiO_x material; also, the amorphous PAA not only effectively binds the active particles together but also envelops each individual SiO_x particle [20].

Charge-discharge studies

Figure 5 illustrates the charge-discharge profiles of Li/ SiO_x -Si-C cells assembled with different binders showing the

1st, 25th, 50th, 75th and 100th cycles. A plateau is visible at around 0.37 V that represents the formation of lithium oxide (Li_2O) and lithium silicate [28]. In the case of Li/ SiO_x -Si-C cell with CMC and CMC: PAA blend binders the plateau was observed around at 0.2 V and it was attributed to high polarization. Figure SI-7 shows the plot of specific capacity as a function of cycle number at 0.1 C-rate with different blend ratios of binder. The initial discharge capacity of Li/ SiO_x -Si-C cell with four different binders are in the following order: 100% PAA (1908 mAh g^{-1}) > PAA: CMC (50:50, 1444 mAh g^{-1}) > PAA: CMC (25:75, 1276 mAh g^{-1}) > and 100% CMC (851 mAh g^{-1}) [Table SI-1]. The large irreversible capacity during its first discharge is attributed to the formation of Li_2O and lithium silicate [29]. Upon cycling the irreversible loss is significantly reduced. It can be noted that the electrode with PAA as a binder delivered the highest discharge capacity. After 100 cycles the Li/ SiO_x -Si-C cell with pure PAA as binder delivered a discharge capacity of 682 mAh g^{-1} with 99% Columbic efficiency which is 2–3 times higher than that of the cells based on CMC and CMC: PAA blends. Finally, the capacity retention values observed for pure PAA and pure CMC binders were calculated as 36% and 12% respectively.

According to Dahn and co-workers [30] the irreversible capacity loss is usually caused by the following: (i) some electrons and lithium ions can be consumed during the

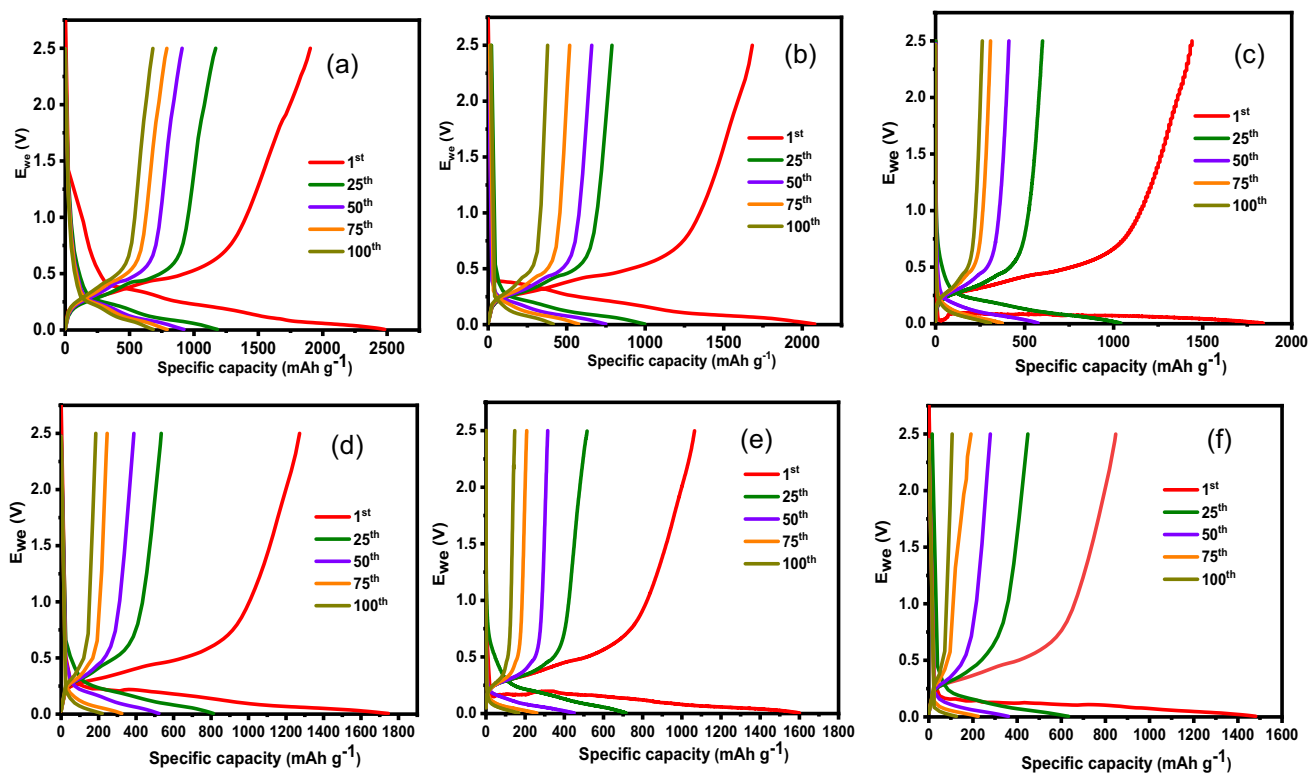


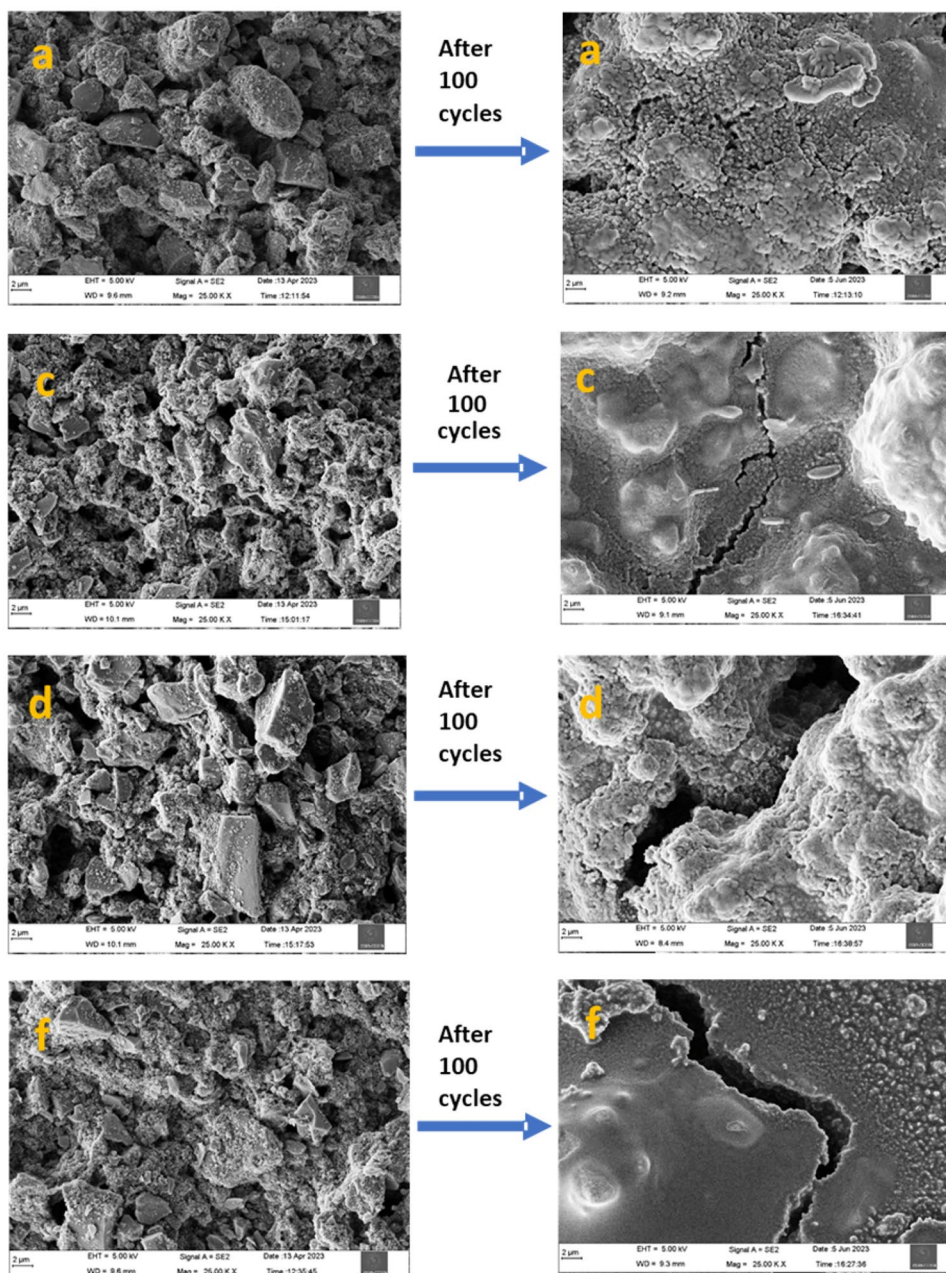
Fig. 5 Charge – discharge profiles of Li/ SiO_x -Si-C cells assembled with electrodes having different blends (please refer Table 1 for the description of the samples)

irreversible formation of the SEI layer on the electrode surface; (ii) trapping of lithium atoms in the silicon particles and (iii) huge volume expansion of the electrode during the first lithiation, that makes the particles to lose their electric contact, which causes permanent capacity loss and thus the performance of silicon-based electrodes is mainly influenced by the nature of the binder. The inferior cycling performance of blend-based polymeric binders can be attributed to the lack of optimal interfacial structure and poor interaction between the polymeric binders and electrolytes and also mechanical properties. Also the condition path way for the migration of lithium-ion may be hindered by the blended polymeric membranes.

FE-SEM analysis

In order to analyze the surface morphology of the $\text{SiO}_x\text{-Si-C}$ electrodes prepared with different binders, FESEM analyses were carried out before and after 100 cycles, and are displayed in Fig. 6. The irregular SiO_x , silicon and carbon particles are homogeneously distributed on the electrode surface before cycling. Upon 100 cycles (alloying/de-alloying) the porosity of the electrode is greatly reduced due to the volume expansion of the silicon particles [20, 31]. Apparently, the $\text{SiO}_x\text{-Si-C}$ cycled with pure PAA exhibited micro cracks while the electrodes with 50,75 and 100% of CMC appear with more cracks in the form of islands in

Fig. 6 FESEM images of $\text{SiO}_x\text{-Si-C}$ electrodes with different blend ratios of PAA and CMC binder before and after cycling. The letters refer to the samples list is shown in Table 1



which the active materials zones are completely separated among them. The results support the fact that the strength, ductility and toughness of the polymeric binders are greatly influenced by the microcrystalline and amorphous regions of the active materials. The polymeric binders are unable to sustain the stress induced by the expansion of SiO_x particles and thus the integrity of the electrode is lost. While comparing the chemical structure of PAA and CMC, the PAA binder offers better interfacial interaction between the binder and SiO_x particles and stronger adhesion between the electrolyte layer and the copper substrate. More importantly, due to the high viscosity of PAA, it may prevent the sedimentation and aggregation of SiO_x and carbon particles during electrode formulation and this enables uniform distribution of electrical conducting network [32, 33]. In general, a very weak binder-electrolyte interaction is considered as a desirable property, which can facilitate for the formation of a deformable but stable SEI on the electrode surface. In the present work, CMC and CMC-added blends show higher affinity towards the solvents, that results in higher electrolyte uptake values, as previously discussed. In PAA, each monomer has carboxyl group that provides stronger hydrogen bonding interaction between binder and SiO_x as well as higher mechanical properties that synergistically offer better electrochemical properties than CMC and CMC-based counterpart.

Electrochemical impedance spectroscopy studies

Electrochemical impedance spectroscopy (EIS) is widely used to probe the electrode kinetics, rate capability and other electrode characteristics of batteries. Figure 7 shows the Nyquist plots of Li/ SiO_x -Si-C cells prepared with different polymeric binders; data refers to cells measured before charge/discharge test, as well as after 50th and 100th cycles at 25 °C. The plots have been fitted using the z-fit software, and the corresponding values are presented in Table 2. The intercept at a high frequency region corresponds to R_s , ohmic resistance, plots also show a semicircle at medium frequency region (R_{ct} , charge-transfer resistance) and an inclined line at low frequency region (Z_s , Warburg impedance) to the real axis respectively. Regardless of the binder used, all Li/ SiO_x -Si-C cells exhibited more or less the same R_s value (5–7 ohms). However, the R_{ct} for the Li/ SiO_x -Si-C cell with poly acrylic acid offers a value of 49 ohms which is lower than that of the Li/ SiO_x -Si-C cell with a CMC binder, indicating a reasonable binder interface for active material and Li-ion interaction to an enhanced electronic and ionic conductivity of the PAA binder as shown in Table 1 [34].

According to Aurbach's groups, the morphology of the silicon-based anode materials is highly critical and it is very tedious to interpret the semicircles without any ambiguity [35]. Generally, the high frequency reveals the surface

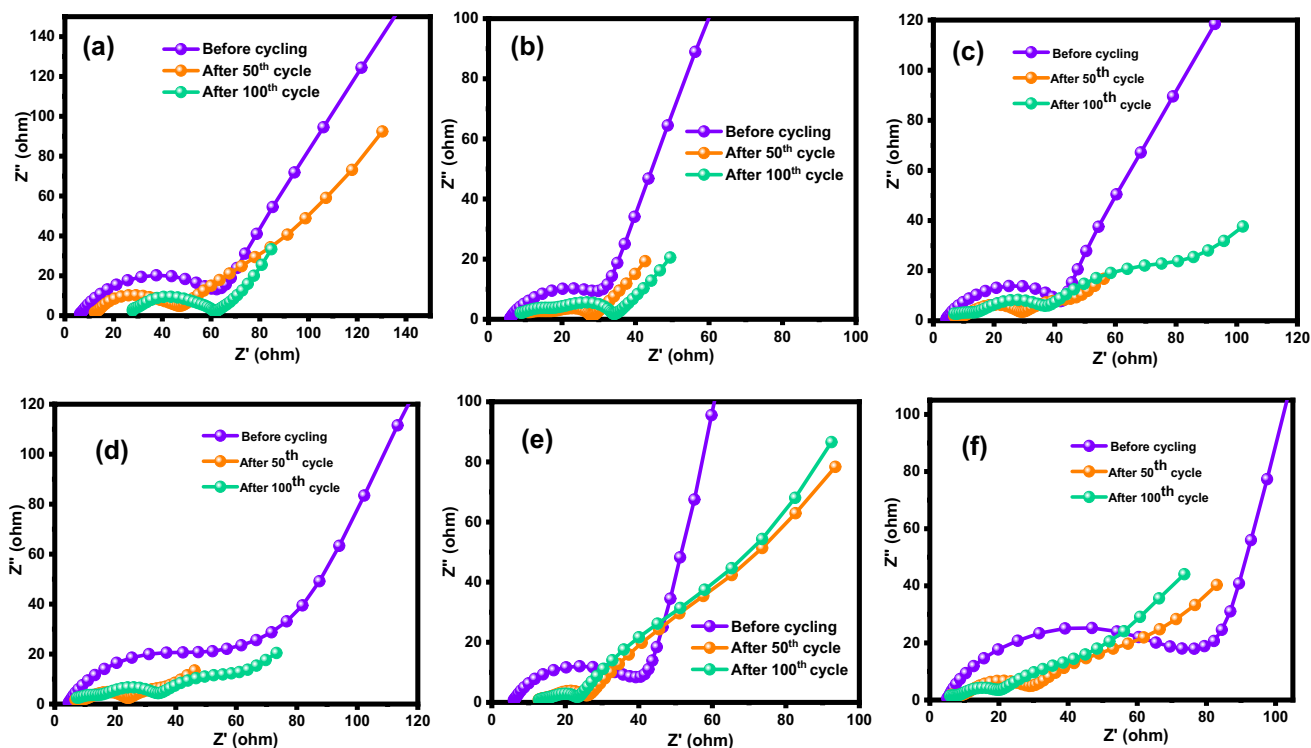


Fig. 7 Nyquist plots of Li/ SiO_x -Si-C cells prepared with different binders. Data were collected after different cycles, while letters refer to the samples list shown in Table 1

Table 2 Impedance values of SiO_x-Si-C with different blend ratios of PAA and CMC binder

Composition	R _s			R _{SEI}			R _{ct}		
	Before	50th	100th	Before	50th	100th	Before	50th	100th
a	4	10	29	-	11	15	49	27	15
b	4	5	5	-	10	11	22	11	15
c	3	4	5	-	7	10	29	18	22
d	3	4	5	-	7	11	36	13	19
e	3	5	13	-	8	8	39	9	5
f	3	4	3	-	6	6	65	17	11

chemistry of Si-based anodes while low frequency indicates the diffusion processes such as solid-state diffusion of lithium ions into silicon materials. At very low frequency, the impedance of the electrodes can represent a capacitive behavior due to the potential-dependent lithium content in the Li-S alloys. Upon cycling, a decrease in the gradient is observed, which shows the diffusion of lithium ions within the SiO_x-Si-C materials [36]. Further, the diameter of the semicircle in the medium-frequency region represents the resistance value of the newly formed SEI layer (R_{SEI}) [37]. Regardless of the type of binder used, the total resistance ($R_s + R_{ct} + R_{SEI}$) of the Li/SiO_x-Si-C cells is reduced after 100th cycles (Table 2). The reduction in impedance is ascribed to the uniform lithiation of the Li/SiO_x-Si-C electrode.

In general, upon cycling an increase in the values of R_{ct} will be observed owing to the pulverization of the silicon particles and the discontinuity between the electrode materials when PVdF is used as binder. On the contrary, in the present study, value of R_{ct} is found to be decreased which indicates that the pulverization of Si particles has been significantly prevented with the added SiO_x particles and the polymeric blend binders. In the PAA, carboxylic groups are present with high concentration and the carboxylic polar units can provide not only better interfacial interaction with SiO_x and Si particles but also stronger adhesion between the electrode layer and copper substrate. Additionally, the high viscosity of PAA solution in water could prevent SiO_x, silicon and Super P carbon black from sedimentation and aggregation, upon the evaporation of the solvent (water) results in the electrode formation of high uniformity. Therefore, the stronger adhesion between current collector and binders ensures good electrical contact of the electrode while cycling, and provides more diffusion paths for ionic transport and electronic conduction for better electrochemical performances.

XPS studies

X-ray photoelectron spectroscopy is widely used in the battery field to investigate the chemical composition of electrodes surface, with the aim of determining the elemental bonding properties. The preliminary overview XPS survey

spectrum showed the presence of carbon, oxygen, silicon and lithium elements before cycling (Fig. SI 8). In the C1s spectrum, characteristic peaks at 284.2, 284.9, 285.1, 286.7, and 288.8 eV correspond to C–C, C–H, C–O, C=O, and COOH/COOR, respectively [38, 39]. The O 1s spectra of the electrode show a peak around 532.7 eV which represents the formation of C–O. A similar trend has been observed for all samples irrespective of the type of binders used (samples c, d and f). The appearance of the metal carbonate peak at 531.5 eV observed for the blended binders is insignificant for the samples prepared with pure PAA and pure CMC [39]. In the case of pure PAA (sample a), the peak seen at 532 eV is assigned to carbonyl or organic C=O [41]. For the Si 2p spectra, the electrodes exhibited peaks at 99.7, 101.9 and 103.5 eV, corresponding to SiO_x, silicon and SiO₂, respectively. The Li 1s spectra showed the peak at around 56 eV corresponding to lithium. Before cycling (Fig. SI 8), no peaks are seen in the nitrogen, fluorine and sulfur spectra.

In order to analyze the formed SEI layers, the XPS spectra of the electrodes prepared with different binders and tested for 100 cycles were collected and are shown in Fig. 8. C 1s spectral region shows peaks at 284.2, 286.1, 287.2, 289.2 and 292.2 eV, corresponding to the C–C, C–O, π - π^0 , C=O and CF₂ bonds, respectively. However, the peaks corresponding to C–C, π - π^0 and C=O disappear when pure CMC was used as a binder. For the O 1s spectra, the electrodes exhibited peaks at 529.6, 530.9 and 532.3 eV, corresponding to metal oxides, metal carbonate and carbonyl or organic C=O, respectively [40]. Apparently for the pure CMC electrode, metal oxides bonding was not observed. As shown in Fig. 8a, c and d, Li 1s spectra of electrode shows a peak at around 54.7 eV which is due to the formation of lithium hydroxide [42], while the Li₂CO₃ signal appears in the electrode prepared with pure CMC (Fig. 8f). Irrespective of the blend ratios between PAA and CMC, the appearance of the F 1s peak at 684 and 687.8 eV is associated with metal fluoride (LiF) and organic fluorides (C–F bonds), respectively. Regardless of the binders used, the peaks observed at 398.7 eV and 166.7 eV represents the formation of Si₃N₄ and Li₂SO₄ respectively.

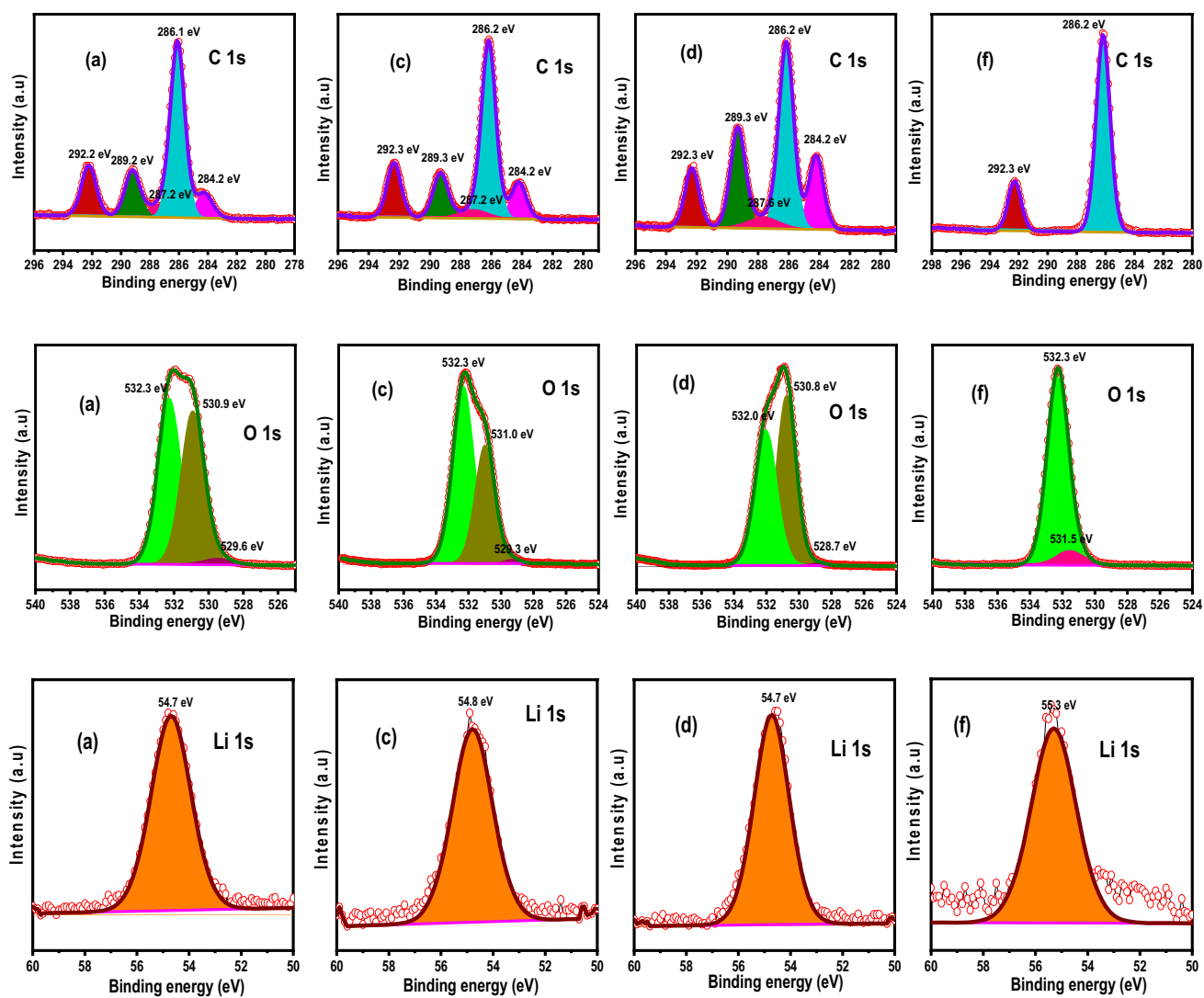


Fig. 8 C 1s, O 1s, Li 1s, F 1s, N 1s and S 2p XPS spectra of $\text{SiO}_x\text{-Si-C}$ with different blend ratios of PAA and CMC binder (a, c, d and f) after 100 cycles

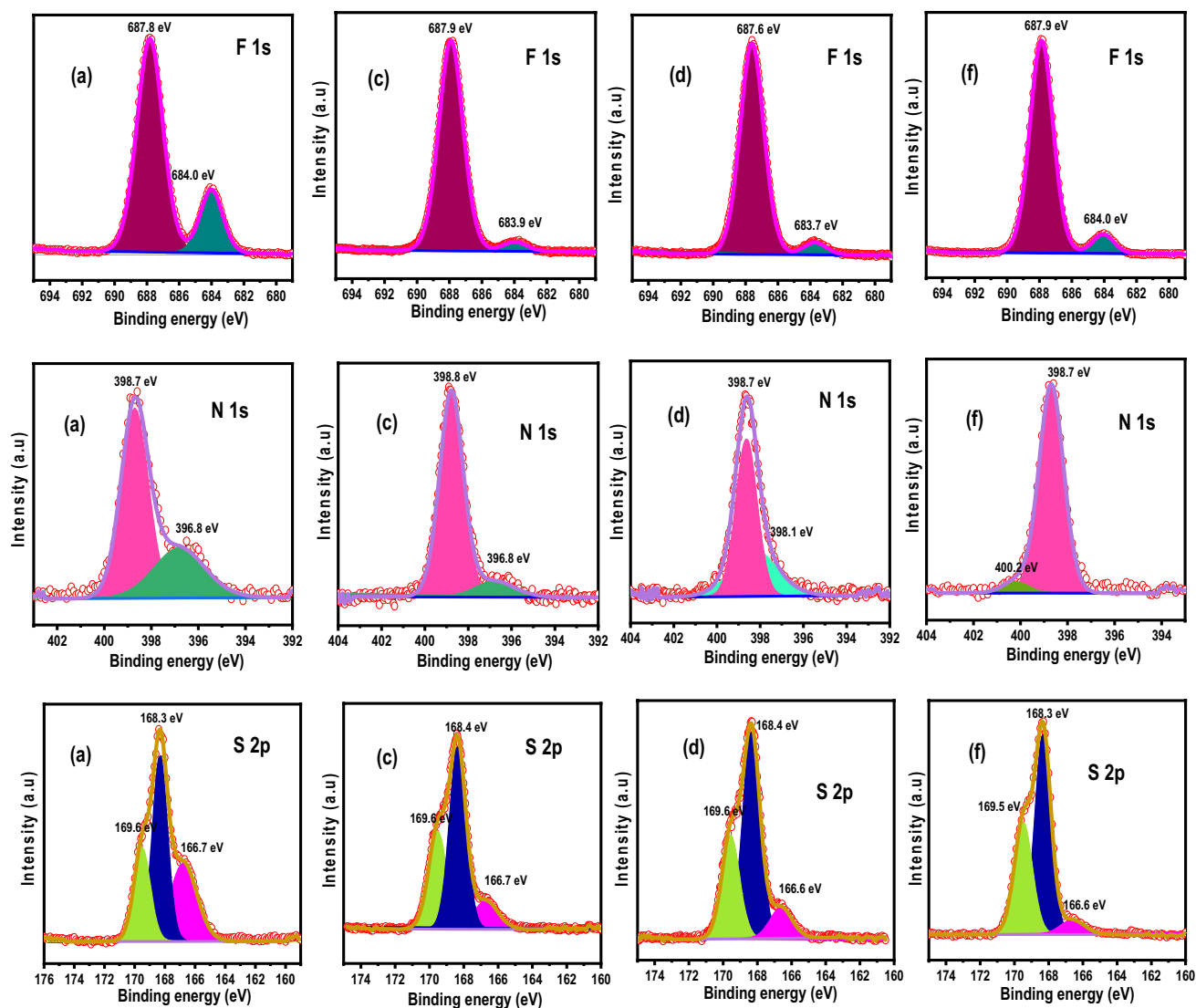


Fig. 8 (continued)

Conclusions

In summary, we have prepared different polymeric blend membranes comprising PAA and CMC by a kneading machine. The prepared membranes were subjected to TGA, FE-SEM, FT-IR and tensile characterization measurement. Also, we investigated the electrochemical and interfacial properties of SiO_x -Si-C composite electrodes before and after being cycled, investigating the effect of several binder formulations. The electrode coated based on pure PAA exhibited superior gluing properties compared to electrodes prepared with other polymeric binders. The charge–discharge studies revealed that the Li/SiO_x-Si-C cell with pure PAA as a binder offered the highest a maximum discharge capacity of 682 mAh g⁻¹ with 99% Coulombic

efficiency and it was attributed to the interaction between carboxyl group of PAA and current collector in addition to its mechanical integrity, low amount of swollen electrolytes and lower R_{ct} value as further substantiated by EIS studies. The XPS studies further confirmed the formation of reductive products such as Li_2CO_3 , LiF and C–F. The structural characteristics of the binder have a major impact on the electrochemical performance of Li-S cells and, therefore, choosing an appropriate binder is a paramount criterion to improve the cycle life and energy density of SiO_x -based anodes.

Further to probe the roles of polymeric binders in the electrodes, powerful tools such as advanced characterizations techniques and modeling studies have to be employed which can improve their surface, electrochemical and mechanical properties. More importantly, natural and water

soluble polymers can offer better environmental responsiveness for future-generation binder systems.

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Declarations

Conflict of interest The authors declare no conflict of interest.

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