Guar Gum: Structural and Electrochemical Characterization of Natural Polymer based Binder for Silicon-Carbon Composite Rechargeable Li-ion Battery Anodes

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Abstract

Long term cyclability of a composite Li-ion anode electrode comprised of 82 wt.% Si/C lithium ion active material along with 8 wt.% polymeric binder and 10 wt.% Super P conductive carbon black has been studied utilizing polymeric binders exhibiting different elastic/tensile moduli and tensile yield strengths. Accordingly electrochemically active Si/C composite synthesized by high energy mechanical milling (HEMM), exhibiting reversible specific capacities of ~780mAh/g and ~600mAh/g at charge/discharge rates of ~50mA/g and ~200mA/g, respectively were selected as the Li-ion active anode. Polyvinylidene fluoride (PVDF) and purified guar gum (PGG) with reported elastic modulus ~1000MPa and ~3200MPa, respectively were selected as the binders. Results show that the composite electrode (Si/C + binder + conducting carbon) comprising the higher elastic modulus binder (PGG) exhibits better long term cyclability contrasted with PVDF. ¹H NMR analysis of the polymer before and after cycling shows structural degradation/deformation of the low elastic modulus PVDF, whereas the high elastic modulus PGG binder shows no permanent structural deformation or damage. The results presented thus suggest that PGG based polymers exhibiting high elastic modulus are a promising class of binders with the desired mechanical integrity needed for enduring the colossal volume expansion stresses of Si/C based composite anodes.

Key words: Binder; Silicon; Li-ion; Anode; Composite

1. Introduction

Rechargeable Li-ion battery (LIB) technology is considered as the frontrunner amongst various electrochemical energy storage (EES) devices due to its high usable specific energy (~100-200 Wh/kg) and high operating (~3V-5V) voltage window [1,2]. Despite considerable advancements, systems meeting the higher energy demand applications are still elusive for complete deployment in plug-in electric vehicles (PEV) or electric vehicles (EV) systems due to the limited energy and power densities [1-4]. In order to further improve the energy density of LIBs to render them amenable for higher energy application ($\geq 300\text{Wh/kg}$), alternative Si based anode materials with an attractive theoretical specific capacity ~4200mA/g representing a ~10-fold increment over the traditionally used graphite anode has been extensively studied in recent

years [1,3,5-11]. The ubiquitous structural disintegration of Si during repeated alloying/de-alloying following colossal volume expansion (~300%), and the resultant capacity fade within few tenths of cycles is universally reported [12-15]. In order to improve the structural stability/integrity as well as the long term cyclability of Si based anodes, nanotechnology and nanoscale architectures have been explored for generating various nanoscale morphologies of Si (*e.g.* nanotube, nanowire, nano-droplet) and nano-composites of Si and C (*e.g.* Si/C nanocomposite) [1,5-19]. Despite much advances, Si based nano-materials or nano-composite electrodes still display structural degradation and limited cyclability with a fade in capacity exceeding 0.1 % per cycle.

Concomitant with the materials development work, there are several published reports demonstrating improvement in the cyclability of Si based active materials by proper design and effective development of composite electrode (active materials + binder + conducting carbon) exploiting the mechanical properties of the binder combined with effective interactions of the binder functional groups with the native silicon oxide layers on the Si surfaces [20-26]. Consequently, during the electrode manufacturing process, a small volume fraction of inactive binder (~2-8 wt.%), facilitating uniform binding of the particles is homogeneously mixed with micron sized electro-active particles (< 40 μ m) along with electronically conductive carbon (CC) (*e.g.* Super P carbon black) to yield a homogeneous slurry. The slurry is then cast onto suitable current collectors of few microns thick to form a particulate composite electrode. The particulate composite electrode generated on a suitable current collector must be structurally and chemically stable during repeated cycling of the electrode for at least a thousand or greater cycles. In the case of the widely used graphitic anode in commercial LIBs, the composite electrode utilize PVDF as a binder displaying excellent cyclability during the charge/discharge processes [27,28].

The mechanical stress/strain generated on graphite as well as the electrode during alloying and dealloying processes with Li-ion (~10% volume change) is expected to lie within the elastic limit of graphite and the composite electrode. Hence the systems do not exhibit any permanent deformation or mechanical degradation of graphite or the intercalated LiC₆ phase [27,28]. However, it is well-known that PVDF commonly used in commercial graphitic anodes, is not suitable for Si based active materials [20-26,29,30]. The tremendous mechanical stress/strain beyond the elastic limit generated within the composite electrode (Si + binder + CC)

results inevitably in plastic deformation of Si based composite electrode causing the well-known mechanical degradation or permanent deformation of the composite electrode leading to loss of contact between the active material with the current collector causing capacity loss in within few tenths of cycles.

Improvement in cycling of Si based composite electrode clearly requires indigenous engineering of the mechanical properties of the composite electrode to achieve optimum elastic modulus, strength and toughness, and low stress/strain on the composite electrode (within the elastic limit) by proper distribution of the generated stress/strain within the composite electrode. It is well known that the mechanical properties (*e.g.* elastic modulus, fracture strength) of the particulate composite electrode and stress/strain distribution within the composite electrode depend on the mechanical properties, which in turn depend on the volume fraction of the binder matrix as well as the dispersed active particles following the Halpin-Tsai equation [31]. In this regard, stiffer (high elastic modulus) binders such as water soluble Na-Carboxymethyl cellulose (Na-CMC), polyacrylic acid (PAA), sodium alginate based binder and different blended polymers have been recently identified as better choices compared to PVDF for Si based system. However, despite the novelty and improved initial performance, they all exhibit degradation over several cycles [20-26,29,30] casting doubts on their long term performance. In the present investigation novel water soluble, biodegradable, non-toxic and good film forming ability of polysaccharide based binders namely, purified guar gum (PGG) obtained after purification of raw guar gum has been studied as a potential binder system for the Si/C nanocomposite electrode system. The biodegradable nature of the system further adds to the possibility of green engineering and the environmentally benign aspect of polymeric binder systems for LIB.

Guar gum is a natural nonionic polysaccharide extracted from the refined endosperm of cluster bean seeds, chemically classified as galactomannan. It is basically composed of a straight chain backbone of D-mannose units, united by β (1-4) glycoside linkages, and bears a single D-galactose side chain unit on approximately every alternate mannose, joined to it by an α (1-6) glycoside linkage (see **Fig. 1**) [32,33] making it an attractive system for exploring as a binder for LIBs as indicated in the present study. In recent publication, gaur gum and its derivative has been reported as a suitable binder for silicon nanoparticles which shows excellent electrochemical performance [34,35]. In the present study, contrary with the published reports, Si/C composite

consisting of more ubiquitous micron-sized Si dispersed on graphite matrix obtained by cost effective high energy ball milling has been used as a Li-ion active material to study the cyclability of the composite electrode (Si + binder + CC) based on PGG binder and Si/C active materials. In addition, fundamental study of the change in molecular structure of the binder during Li-ion cycling determined by proton nuclear magnetic resonance (^1H -NMR) of PGG along with PVDF before and after electrochemical cycling has been reported in this article. The Si/C Li-ion active materials, synthesized by high energy mechanical milling (HEMM) as reported by the present authors in earlier publications [16,36] exhibiting a reversible capacity $\sim 780\text{mAh/g}$ at C rate of C/16 ($\sim 50\text{mA/g}$) has also been selected as the electrochemically active anode system for this study.

2. Experimental Section

2.1 Materials Synthesis

Mixtures of elemental powders of synthetic graphite (Aldrich, 1-2 μm), Si (Alfa aesar, -325 mesh) and poly-acrylonitrile (PAN) ($M_w \sim 150,000$, Aldrich) of elemental composition 56 wt.% Gr-14 wt.% Si-30 wt.% PAN were subjected to high energy mechanical milling (HEMM) in a high energy shaker mill (SPEX CertiPrep 8000 M) up to 10 h in a stainless steel (SS) vial using 20 SS balls of 2 mm diameter ($\sim 20\text{ g}$) with a ball to powder weight ratio 10:1. Specifically, 0.6 g of PAN was dissolved in $\sim 8\text{ ml}$ N-methylpyrrolidone (NMP) to form a homogeneous solution. Graphite ($\sim 1\text{ g}$), Si ($\sim 0.4\text{ g}$), and the PAN solution were batched in a vial inside an argon filled glove box ($\sim 10\text{ ppm}$ oxygen and $\sim 0.10\text{ ppm}$ moisture) in order to prevent oxidation of the reactive Si components during milling. Decomposition of PAN to form PAN-based carbon (PAN-C) [16,36] was obtained by isothermally annealing the mechanically milled powders at $\sim 973\text{K}$ for 6 h in an ultrahigh purity argon (UHP-Ar) atmosphere using a heating rate of 10K min^{-1} and a flow rate of 100mL min^{-1} . The Si/C, Li-ion active composite powder obtained after thermal treatment at $\sim 973\text{K}$ is further intentionally ball milled for 2 min to destroy the composite inherent structure which is expected to shows inferior cyclability/stability in comparison to the heat treated Si/C composite.

Commercial dried PVDF powder ($M_w \sim 534,000$, Aldrich) was dissolved in anhydrous NMP (N-methyl-2-pyrrolidone, Aldrich) to prepare a 5 wt% PVDF solution. On the other hand, raw gaur gum (Aldrich) was purified via Soxhlet extraction with ethanol following the method described by Cunha *et al.* [37]. Accordingly, Guar gum (20 g) was treated by Soxhlet extraction with ethanol for four days. The obtained product was then hydrated in distilled water (1000 mL) and mixed via magnetic stirring for 4 h, followed by centrifugation at 2000 rpm for 25 minutes. The supernatant was then precipitated in acetone, filtered and washed with ethanol three times followed by vacuum drying. The dried PGG powder has been dissolved in high purity deionized water to prepare a 5 wt% PGG solution. The above mentioned stock solution of PVDF and PGG has been used to prepare the composite electrode with Si/C as Li-ion active material containing Super P as the conductive carbon. **Table 1** shows the reported molecular weight and mechanical properties (film based) of PVDF and PGG binders used for this study [32,38-40]. The reported mechanical properties of PVDF and PGG have been measured using ASTM D882 method.

The composite electrodes were prepared by mixing 82 wt.% of the active Si/C powder of -325 mesh ($<44\mu\text{m}$) and 10 wt.% Super P (SP) conductive carbon black (TIMCAL). The binder solution corresponding to ~8 wt.% binder with respect to the electrode composition is added to the mixture to form a slurry. The as prepared homogenous slurry was then coated onto a Cu foil and dried at 110°C under vacuum for 24h. Circular disc of $\sim 1\text{cm}^2$ area was cut from the dried foil to contain a Si/C active materials loading in the range $\sim 3.0\text{-}3.5\text{ mg cm}^{-2}$ irrespective of binder used.

2.2 Materials Characterization

In order to perform qualitative phase analysis, the milled powders as well as heat treated powders were characterized by X-ray diffraction (XRD) using the Philips XPERT PRO system employing the Cu K_α ($\lambda = 0.15418\text{ nm}$) radiation. To investigate the microstructure of the as prepared Si/C composites as well as the electrochemically cycled electrode, scanning electron microscopy (SEM) analysis was conducted. Quantitative elemental analysis and distribution of the elements (by X-ray mapping) in the Si/C composite was further investigated using the energy dispersive X-ray (EDS) analyzer attached with the SEM. Philips XL-30FEG equipped with an

EDS detector system comprised of an ultrathin beryllium window and Si(Li) detector operating at 25 kV was employed for the secondary electron (SE) image, elemental and X-ray mapping analyses. Fourier Transform Infrared (FTIR) spectroscopy measurements has been performed using a Thermo-Nicolet (Thermo Electron Corporation, USA) FTIR spectrometer. All samples have been analyzed in the attenuated total reflectance (ATR) mode using a Diamond ATR accessory. For each spectrum 32 scans were collected at a resolution of 4cm^{-1} from 4000cm^{-1} to 500cm^{-1} . ^1H -NMR analysis has also been conducted on the PVDF and PGG binders before and after the electrochemical cycling tests to understand the change in molecular structure of the polymeric binder during electrochemical cycling. The PGG binder in the pure form has been dissolved in deuterium oxide (D_2O), whereas PVDF in the pure form has been dissolved in dimethyl sulfoxide (DMSO-d_6) with a concentration of 5 mg/ml for conducting the ^1H -NMR study. The NMR spectra collected for PGG and PVDF in the pure form has been considered and referred to as before cycling spectra. On the other hand, the composite electrode obtained after 111th cycle has been washed thoroughly with Dimethyl carbonate (DMC) solvent to remove any electrolyte and other soluble species. The PGG and PVDF binder was then isolated from the washed cycled electrode following dissolution in the respective solvents, e.g. PGG+Si/C+SP in deuterium oxide (D_2O) and PVDF+Si/C+SP in dimethyl sulfoxide (DMSO-d_6). The solution containing the soluble binder is then separated from Si/C+SP particles by filtration and subjected to ^1H -NMR analysis. The ^1H -NMR spectra of all the binders considered in this study in the pure form (considered as before cycling) and after electrochemical cycling have been recorded by Bruker Avance III 700 MHz NMR spectrometer using a TXI probe. All of the ^1H -NMR spectra have been collected with 16 to 32 scans at ambient temperatures.

Electrochemical characteristics of the composite electrodes were determined on electrodes that were prepared by mixing 82 wt.% of the active powder of -325 mesh, 10 wt.% Super P carbon (SP) and 8 wt.% binder. A 2016 coin cell design was used by employing lithium foil as the counter electrode, the Si/C composite as the working electrode and 1M LiPF_6 in ethylene carbonate/diethyl carbonate ($\text{EC/DEC} = 1:2$ in volume) as the electrolyte. All the cells tested in this study were cycled at room temperature ($\sim 298\text{ K}$) in the voltage range from ~ 0.02 to $\sim 1.2\text{V}$ employing different discharge/charge rates ($\sim 50\text{-}200\text{mA g}^{-1}$) and a minute rest period between the charge/discharge cycles using a potentiostat (Arbin electrochemical instrument). Electrochemical impedance spectroscopy (EIS) has been performed on the Versastat 3 (Princeton

Applied Research Inc.) over a frequency range of 0.01Hz-100kHz. An A.C. amplitude of 5 mV was used and the spectra were obtained before cycling and subsequent to the 1st cycle discharge (Li^+ alloying) and charge states (Li^+ de-alloying), and in the charged state after the 20th, 40th and 80th cycle, respectively. The electrode potential was stabilized after charge/discharge cycles and EIS was performed in order to understand the charge storage behavior upon cycling. The effect of cycling on the electrode interfacial resistance and charge transfer parameters has been analyzed by performing equivalent circuit modeling using the Z-View software (Scribner Associates, Inc.; version 3.3).

3. Results and discussion

FTIR analysis was conducted on the PVDF and PGG binders to identify the different functional groups present in the studied polymer binder and also confirm their chemical structure. Accordingly, the spectra obtained from PGG and PVDF shown in **Fig. 1** were analyzed. The FTIR spectrum of PGG shows the presence of a very strong and broad absorption band at 3287 cm^{-1} which can be assigned to stretching of the O-H bond, while the sharp absorption band at 2916 cm^{-1} can be attributed to stretching vibrations corresponding to the C-H bond in the CH groups. The bending of C-H bond in CH_2 group is assigned to an absorption band located at 1420 cm^{-1} and the bending of C-O in $\text{CH}_2\text{-O-CH}_2$ group appears in the 1016 cm^{-1} frequency region. On the other hand, the absorptions of the FTIR spectrum of PVDF indicate that the crystalline phase is present in both, α and β conformations. The signals at 1401, 1178, 1066, 877, 840, 532 and 485 cm^{-1} were attributed to the β conformation and the bands at 975, 796 and 614 cm^{-1} were assigned to the α conformation. The other signals in the spectrum correspond to the vibrations arising from the amorphous phase of the polymer. These results are in good agreement with the FTIR signal characteristics already described in the literature for PGG and PVDF [32,33,41].

The XRD patterns of Si/C composite obtained from the 56wt.% Gr-14 wt.% Si-30 wt.% PAN precursor after 10h of mechanical milling followed by thermal treatment at $\sim 973\text{K}$ in Ar atmosphere are shown in **Fig. 2a**. As shown in **Fig. 2a**, the XRD patterns of the 10h milled sample as well as the heat treated powder show the presence of graphite and silicon without any detectable amount of unwanted SiC, similar to our earlier publications [16,36]. The composition of the Si/C is estimated based on the 37% yield of PAN-C [16] and no weight loss of Si and

graphite based on the thermal DSC/TGA analysis yielding approximately C-17.2 wt.% Si. The secondary electron (SE) SEM image of heat treated sample obtained after heat treatment at $\sim 973\text{K}$, shown in **Fig. 2b**, indicates the formation of irregularly shaped fine particles ($<0.5\ \mu\text{m}$). Elemental analysis using energy dispersive X-ray spectroscopy, shown in **Fig. 2c**, indicates the presence of C, Si and iron (Fe) in the Si/C active materials. Appearance of the Fe peak in the EDS (**Fig. 2c**) analysis mainly arises from the iron contamination in the milled sample due to the SS milling media used causing frictional wear following impingement of the harder Si and graphite particles with the relatively soft SS balls and the SS walls of the container. In order to determine the distribution of the C and Si, elemental X-ray mapping has been used and the result is shown in **Fig. 2d** and **2e**. The elemental X-ray maps of C and Si combined with the SE image (**Fig. 2b**) show that the electrochemically active Si particles are homogeneously dispersed and distributed on the graphite matrix. During high energy mechanical milling of graphite and silicon, it can be expected that the harder silicon particles gets fragmented and embedded within the graphite matrix.

Figure 3a shows the variation of gravimetric specific capacity (mAh/g) with cycle number for the Si/C + PVDF + SP composite electrode, made with 8 wt.% PVDF binder, cycled at different current rates (50mA/g to 200mA/g) and an electrode loading of $3.0\text{-}3.5\ \text{mg cm}^{-2}$. The Si/C+PVDF+SP composite electrode cycled at $\sim 50\text{mA/g}$ for the 1st two cycles shows a first discharge (Li^+ alloying) and first charge (Li^+ dealloying) capacity $\sim 990\text{mAh/g}$ and $\sim 780\ \text{mAh/g}$, respectively, with a first cycle irreversible (FIR) loss of $\sim 21\%$. On the other hand, the Si/C+PVDF+SP composite electrode cycled at $\sim 100\text{mA/g}$ (3rd-6th cycle) and $\sim 200\text{mA/g}$ (7th-11th cycle) shows a reversible specific capacity $\sim 700\text{mAh/g}$ and $\sim 620\text{mAh/g}$, respectively (**Fig. 3a**). The differential capacity plot (dQ/dV vs. V) of Si/C+PVDF+SP composite electrode corresponding to the 1st and 2nd cycle cycled at $\sim 50\text{mA/g}$, shown in **Fig. 3b**, shows that both Si and graphite are electrochemically active to Li, as expected. The appearance of alloying peaks corresponding to $\sim 0.3\text{V}$, $\sim 0.25\text{V}$ and $\sim 0.09\text{V}$ after the first cycle suggests the formation of LiSi , Li_7Si_3 and $\text{Li}_{3.16}\text{Si}$, and amorphization of Si after the first cycle, as discussed in detail in our earlier papers [42]. In order to study the long term cyclability of the composite electrode, which primarily depends on the mechanical stability/integrity of the electrode structure as well as electrode impedance/resistance during repeated alloying and de-alloying processes, the Si/C+PVDF+SP composite electrode is cycled for an additional 100 cycles at a current rate of

~200mA/g. The long term cyclability of the Si/C+PVDF+SP composite electrode, shown in **Fig. 3a**, reflects the degradation of the specific capacity with increasing cycle numbers (fade in capacity ~0.22% per cycle), depicting a specific capacity ~466mAh/g after the 111th cycle. The composite electrode also exhibits a coulombic efficiency ~99.5% in the entire range of cycling. This fade in capacity likely arises due to partial mechanical degradation of the composite electrode caused by the degradation of the binder matrix rather than the failure of individual Si/C particle and corresponding increase in the electrode resistance with cycling as measured by electrochemical impedance spectroscopy detailed later.

The SEM images before and after cycling of the composite electrode (shown in **Fig. 4**) shows no significant structural damage/mechanical disintegration of the composite electrode after cycling. However, the fine structural degradation or integrity of the binder cannot be unequivocally confirmed from these SEM images. In order to confirm and understand the molecular level degradation or integration of the PVDF matrix binder, the chemical structure of PVDF polymer before and after electrochemical cycling has been characterized by ¹H NMR. The ¹H NMR spectrum of PVDF before cycling, shown in **Fig. 5a**, indicates a broad resonance in the range of δ ~2.8-3.0 ppm corresponding to the PVDF polymer attributable to the head-to-tail (ht) bonding arrangements of the PVDF main chains, whereas the weaker chemical shift at δ ~ 2.25 ppm is assigned to the head-to-head (hh) or tail-to-tail (tt) stereo-regularities [43,44]. The chemical shift at ~2.50 ppm corresponds to the residual DMSO-d₆ signal. The broad resonance in the range of δ ~2.8-3.0 ppm corresponding to PVDF is not seen after electrochemical cycling (**Fig. 5b**) which indicates possible degradation or permanent deformation of the low elastic modulus PVDF polymer during electrochemical cycling. The additional peaks at different δ values after electrochemical cycling (**Fig. 5b**) are expected to arise due to the presence of smaller degraded species of PVDF and/or other organic byproducts generated due to electrolyte decomposition on the surface of the electrode. This result clearly suggests the inferior structural characteristics of the PVDF based soft polymer binder rendering it clearly unfavorable as a polymer binder system for Si based anodes. The inferior stability and structural changes of PVDF following cycling depicted by the ¹H NMR analysis is indicative of the inability of PVDF to support the Si/C nanocomposite particles resulting in failure of the Si/C based electrodes

system even with a low Si content exhibiting a specific capacity of only ~600mAh/g when cycled at ~200mA/g.

The ^1H NMR results indicate that the use of a higher modulus polymer would bode better and lead to likely better performance compared to PVDF. In order to improve the bond strength, and as a result, the tensile modulus of the polymeric binder, water soluble natural polymer PGG of higher elastic modulus and yield strength than PVDF (**Table 1**) is used to improve the cyclability of Si/C based composite electrode. **Fig. 6** shows the variation in specific capacity versus cycle number of Si/C+PGG+SP composite electrode with an identical active material loading of $3.0\text{--}3.5\text{ mg cm}^{-2}$, fabricated with 8 wt.% water soluble PGG binder, cycled at different current rates (50mA/g to 200mA/g) but similar to the composite made with the PVDF binder discussed earlier. The Si/C+PGG+SP composite cycled at ~50mA/g for 1st two cycle shows similar first discharge and first charge capacity ~1006mAh/g and ~777 mAh/g, respectively, with an irreversible loss of ~23% in comparison with PVDF binder. The Si/C+PGG+SP composite electrode cycled at ~100mA/g (3rd-6th cycle) and ~200mA/g (7th-11th cycle) also shows comparable reversible capacity ~700mAh/g and ~620mAh/g, respectively, in comparison to PVDF binder under identical conditions (**Fig. 3a**). The above results clearly suggests that the different physical/chemical properties of the composite electrode with PGG binder such as wettability/permeability of the electrolyte, Li ion transport, electronic conductivity is not affected by the PGG binder. However, the long term cyclability of the Si/C+PGG+SP composite electrode, shown in **Fig. 6**, clearly indicates improved cyclability (fade in capacity ~0.04% per cycle) in comparison to the Si/C+PVDF+SP composite electrode (fade in capacity ~0.22% per cycle), and exhibits a capacity ~600mAh/g after 111th cycle. Moreover, the Si/C+PGG+SP composite electrode displays a coulombic efficiency ~99.5% in the entire range of cycling.

^1H -NMR studies of PGG containing electrode before and after cycling has also been performed to understand the structural stability of the binder. The ^1H -NMR spectra of PGG before cell cycling is shown in **Fig. 7a**. The broad resonances in the region $\delta = 3.0\text{--}4.2\text{ ppm}$ are due to sugar protons and a peak at $\delta = 4.7\text{ ppm}$ corresponds to the anomeric protons, overlaid by the solvent peak ($\text{D}_2\text{O-d}$) [32]. The ^1H -NMR spectra after cell cycling (**Fig. 7b**) shows that PGG does not degrade (peaks are marked as *) even after 111th cycle, which suggest that the high elastic modulus binder based on PGG can act as suitable binders in comparison to PVDF. The

additional peaks at different δ values after electrochemical cycling (**Fig. 7b**) are expected to arise due to the presence of different dissolved organic byproducts generated due to decomposition of the electrolyte on the electrode surface that are likely soluble in the solvent used to extract the binder.

In order to understand the failure behavior of PVDF and PGG based binder electrode, electrochemical impedance spectroscopy of Si/C+PVDF+SP and Si/C+PGG+SP composite electrodes have been performed using 5 mV AC amplitude at various stages of cycling to measure the change of interfacial and charge transfer resistance with cycling. A representative impedance curve obtained after the 80th cycle of charge (Li-alloying at 1.2V) of Si/C+PGG+SP composite electrode, shown in **Fig. 8a**, shows the characteristic three semi-circular arcs at high and medium frequency, and series resistance (R_s) of $\sim 4\text{-}5 \text{ } \Omega\text{-cm}^2$ [11,43,44]. The high frequency 1st and 2nd semi-circular arc is associated with interfacial impedance between the active material and current collector (R_{ec}), and surface films due to the solid electrolyte interphase (SEI) formation between the electrode and electrolyte (R_{film}), respectively [43,44]. The combined impedance of R_{ec} and R_{film} has been denoted as interfacial resistance ($R_{int} = R_{ec} + R_{film}$) in the present work. The 3rd semi-circular arc in the medium frequency region corresponds to the electrode charge transfer resistance (R_{ct}) [45,46]. Low frequency Warburg type behavior (W_o) is also observed corresponding to the solid-state Li diffusion. Randle's circuit model, shown in the inset of **Fig. 8a**, has been used to fit the curves in the Nyquist plots to obtain the R_s , R_{ec} , R_{film} , R_{int} ($=R_{ec}+R_{film}$) and R_{ct} resistances.

Figure 8b depict the Nyquist plot as well as fitted curve of the Si/C+PVDF+SP electrodes and Si/C+PGG+SP electrodes measured at open circuit potential (OCP). The experimental curve obtained at OCP has been fitted by considering R_s and interfacial resistance ($R_i=R_{ec}+R_{film}$) since R_{ec} and R_{film} could not be distinguished as a separate arc, and the values of R_s and R_i are tabulated in **Table 2**. The electrochemical impedance spectroscopy of Si/C composite with PVDF and PGG shows comparable interfacial resistance ($R_i \sim 200 \text{ } \Omega\text{-cm}^2$) at OCP (**Fig. 8b** and **Table 2**). On the other hand, the impedance curve after 1st discharge (0.02V-1st

cycle) along with the fitted curve, shown in **Fig. 8c**, clearly shows reduction in the interfacial resistance (R_i) in comparison to OCP (**Table 2**) as expected with the formation of lithium silicides during discharge. However, the interfacial resistance (R_i), at 0.02V in the discharged state, is lower for Si/C+PGG+SP ($75 \text{ } \Omega\text{-cm}^2$) compared to Si/C+PVDF+SP ($97 \text{ } \Omega\text{-cm}^2$) (**Table 2**) which suggests the formation of a larger interphase/SEI layer formation for the Si/C+PVDF+SP composite electrode contrasted with that for the Si/C+PGG+SP composite electrode. This result clearly suggests that the Si/C+PVDF+SP composite electrode undergoes more degradation after the 1st discharge than Si/C+PGG+SP composite electrode. **Figures 8d, 8e and 8f** depict the Nyquist plots along with fitted curves for the Si/C+PVDF+SP electrodes and Si/C+PGG+SP electrodes after the 1st charge (1.2 V-1st cycle), after the 20th cycle charge (1.2 V - 20th cycle) and after the 40th cycle charge (1.2 V-40th cycle), respectively. **Table 2** lists the values of R_s , $R_i=R_{\text{film}}+R_{\text{ec}}$ and R_{ct} obtained from the fitted curves. It can be noticed that the R_i decreases upon further delithiation after the 1st cycle (**Table 2**) and remains constant with increase in cycle numbers. The interfacial resistance after de-alloying of Li at 1.2V after the 1st cycle, 20th cycle and 40th cycle also shows that the Si/C+PGG+SP exhibits lower interfacial resistance ($\sim 10\text{-}12 \text{ ohm-cm}^2$) in comparison to the Si/C+PVDF+SP composite electrode ($\sim 25\text{-}27 \text{ ohm-cm}^2$) (**Table 2**) which shows the effectiveness of the PGG binder for the Si/C electrochemically active composite materials. In addition, it has been noticed that the charge transfer resistance (R_{ct}) of Si/C+PVDF+SP increases with cycle numbers while the R_{ct} values of Si/C+PGG+SP remains almost constant at $\sim 8\text{-}9 \text{ ohm cm}^2$ (**Table-2**). At the same time, the R_{ct} values of Si/C+PVDF+SP are higher than Si/C+PGG+SP. The higher interfacial and charge transfer resistance of PVDF binder probably arises due to the structural failure of PVDF based electrodes whereas PGG shows low interfacial and charge transfer resistances due to better structural integrity with cycle numbers based on the EIS and ^1H NMR analyses.

The above results clearly suggest that the binders based on PGG, exhibiting high elastic modulus (**Table 1**), is useful to improve the mechanical properties of the composite electrode and consequently, the cyclability of Si/C based Li-ion active system. In this regard, the PGG binder exhibiting potentially improved structural integrity of the composite electrode can be named as “mechanical integrity binder (MIB)” whereas the binder used to bind the particles without significant improvement in mechanical properties can be named as a “cohesive binder (CB)” (*e.g.* PVDF). In order to keep the integrity of the composite electrode structure of Si/C

based systems, the generated strain/stress on Si/C particles during alloying and de-alloying processes must be transmitted to the mechanical integrity binder without delamination in such a manner that the strain on the binder (ϵ_b) is equal to the strain of the Si/C particle ($\epsilon_{Si/C}$) and the composite (ϵ_{com}) ($\epsilon_{com} = \epsilon_b = \epsilon_{Si/C}$). In the iso-strain condition, the elastic modulus (E_{com}) and breaking strength ($\sigma_{com.b}$) of the composite electrode will depend on the volume fraction, elastic modulus, breaking strength of the binder and dispersoid Si/C particles following the Halpin-Tsai equation which can predict the micromechanics of particulate composite [31]. The mechanical integrity binder with higher elastic modulus will result in a composite electrode of higher elastic modulus and higher strength. However, it must be mentioned that the stress/strain experienced by the composite electrode ($\sigma_{com}/\epsilon_{com}$) must be within the elastic limit ($\sigma_{com} < \sigma_{com.b}$) to avoid disintegration due to plastic or permanent deformation and consequent degradation of the composite electrode. In order to achieve minimum stress/strain (within the elastic limit) with suitable elastic modulus of the composite electrode with non-permanent deformation, a novel structural design along with suitable mechanical binder integrity needs to be explored. In the present study, it has been identified that the PGG based polymer of elastic modulus ~ 3200 MPa is likely a suitable polymer belonging to the mechanical integrity binder family for Si/C based anode of low Si content exhibiting a specific capacity ~ 600 mAh/g (at ~ 200 mA/g), since the composite electrode stress/strain is expected to be within the elastic deformation region. In addition to improving the mechanical properties, recent investigations have also revealed that the polymeric binders containing carboxylic acid and/or hydroxyl functional groups may improve the cycling performance utilizing hydrogen bonding interactions with the Si active system [20-26]. It must be mentioned here that the high elastic modulus composite electrode also has the disadvantage of being brittle once the stress/strain reaches above breakpoint strength/strain level ($\sigma_{com} > \sigma_{com.b}$). It has also been identified by the present authors (data not shown) that the stiff high elastic modulus polymer binder (e.g. PGG) is not suitable for Si/C composite with high Si content Si/C system (specific capacity ≥ 1200 mAh/g at 100 mA/g) which is expected to exhibit higher mechanical stress/strain on the composite. For higher Si content composite electrode, a blend polymer with higher mechanical properties than the parent polymers needs to be developed. The electrochemical performance of Si/C system based on such blend polymers is currently being explored in the authors' laboratory and the cyclability results will be published in a subsequent publication.

4. Conclusion

The effect of mechanical properties of a mechanical integrity binder on the structural stability and long term cyclability of Si/C based active materials for Li-ion batteries has been studied. Binders belonging to the mechanical integrity binder (MIB) class used for electrode manufacturing processes not only helps to bind the electro-active particles together but is also expected to likely improve the overall mechanical properties of the composite electrode. In the present investigation, two different polymeric binders of different mechanical properties (*e.g.* elastic modulus, yield strength) have been studied to correlate the cyclability of the composite electrode with the mechanical properties of the binder. In this regard, PVDF of elastic modulus $\sim 1000\text{MPa}$, and a novel new polymer family namely, Guar Gum of elastic modulus $\sim 3200\text{MPa}$ has been chosen and explored as a suitable binder for Si/C system. The Si/C, obtained after mechanical milling of Si, Gr, and PAN of nominal composition Gr-14wt.% Si-30wt.% PAN followed by thermal treatment at 973K in UHP-Ar atmosphere, exhibits a specific capacity $\sim 780\text{mAh/g}$ and $\sim 620\text{mAh/g}$ at charge/discharge rate of $\sim 50\text{mA/g}$ and $\sim 200\text{mA/g}$, respectively, irrespective of the binder suggesting that the chosen binder does not affect the Li-ion diffusivity, permeability of electrolyte, electronic conductivity, and other physical properties which can adversely affect the battery performance. However, it has been identified that the long term cyclability of Si/C system depends largely on the binder mechanical properties. Accordingly, the high elastic modulus PGG shows better cyclability than low elastic modulus PVDF binder indicating that the mechanical stress/strain generated within the composite electrode with PGG binder is within the elastic regime. The ^1H -NMR based molecular structural studies of the polymer binders before and after cycling have confirmed that structural degradation of the low elastic modulus PVDF after cycling ensues, whereas the high elastic modulus PGG shows no such permanent deformation or structural damage. These results indicate and suggest that the high elastic modulus PGG based polymer is indeed a promising binder family for Si/C based anode that is worthy of further detailed examination in a full cell assembly.

Author contribution

M.K.D., R. K. and P. N. K devised the original concept and designed the experiments. R. K. and M. K. D. synthesized the materials, prepared the electrodes and performed the electrochemical characterization. K. D. conducted the ^1H -NMR and analyzed the NMR data. M.K. D. and P. H. J. collect and analyzed the impedance data. R.K, B. G., P. M. S, P. P. and S. D. performed SEM and XRD analyses. M. K. D., R. K., K. D., P. H. J. and P. N. K. analyzed the data and wrote the first draft of the paper; and all authors participated in the manuscript revision. The project is conceived and supervised by P.N.K.

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Table -1: Molecular weight and mechanical properties such as tensile modulus (E), tensile yield strength (σ_y) and elongation at break (ϵ_f) of PVDF and PGG polymeric binder [32,33,38-40].

Polymer	M_w	E (MPa)	σ_y (MPa)	ϵ_f (%)
PVDF	534,000	700-1200	20-35	150-350
PGG	1,000,000-2,000,000	3000-3700	32-48	2-4

Table 2: Evolution of interfacial resistance and charge-transfer resistance of Si/C+PVDF+SP composite electrodes and Si/C+PGG+SP composite electrodes with cycling.

	$R_s (\Omega\text{-cm}^2)$		$R_i (\Omega\text{-cm}^2)$		$R_{ct} (\Omega\text{-cm}^2)$	
	PVDF	PGG	PVDF	PGG	PVDF	PGG
OCP	2.06	2.39	188.30	190.30	-	-
0.01 V-1 st cycle	2.37	1.63	96.17	74.66	-	-
1.2 V-1 st cycle	2.24	3.73	25.67	12.08	9.08	9.20
1.2 V-20 th cycle	5.99	2.74	25.27	11.02	10.04	8.22
1.2 V-40 th cycle	2.51	3.48	25.03	11.28	14.07	8.09

Figures Caption:

Fig. 1: FTIR spectra of commercial PVDF and purified Guar Gum (PGG) along with their chemical structures.

Fig. 2: (a) XRD patterns of 50wt.% Gr-20wt.% Si-30wt.% PAN after 10h of milling, and after thermal treatment of mechanically milled powder at 973K for 6h under UHP-Ar atmosphere. SEM secondary electron image (b), EDAX spectra of Si/C composite (c) showing the presence of Si, C and Fe, (d) X-ray elemental map of C and (e) Si of Si/C composite.

Fig. 3: (a) Specific capacity *vs.* cycle number of Si/C+PVDF+SP composite electrode cycled at a constant current of ~50mA/g, 100mA/g and 200mA/g in the potential window 0.02V-1.2V showing the long term cycling response. (b) Differential capacity *vs.* cell potential curves of Si/C+PVDF+SP composite electrode obtained after 1st and 2nd cycle cycled at ~50mA/g in the potential window of 0.02–1.2 V.

Fig. 4: SEM micrograph of Si/C+PVDF+SP composite electrode (a) before and (b) after cycling for 111 cycles.

Fig. 5: ¹H-NMR spectra of PVDF (a) before and (b) after cycling for 111 cycles in DMSO-d₆.

Fig. 6: Specific capacity *vs.* cycle number of Si/C+PGG+SP composite electrode cycled at current rates of 50 mA/g-200 mA/g in the potential window of 0.02-1.2V.

Fig. 7: ¹H-NMR spectra of PGG (a) before and (b) after cycling for 111 cycles in D₂O.

Fig. 8: A representative electrochemical impedance spectroscopy (a) of Si/C+PGG+SP after 80th cycle of charge shows the characteristic impedance at high, medium and low frequency region. Electrochemical impedance spectroscopy of Si/C+PVDF+SP and Si/C+PGG+SP composite electrode b) at open circuit potential, c) after 1st discharge at ~0.02V, d) after 1st cycle charge at 1.2V, e) after 20th cycle charge at 1.2V, and f) after 40th cycle charge at 1.2V.

Absorbance (a.u.)

(d)

100 μm

100 μm

(e)

100 μm

100 μm