

Silicon-doped Carbon Xerogel with poly(sodium 4-styrenesulfonate) as a Novel Protective Coating and Binder

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Abstract

A composite anode comprised of silicon impregnated in a conductive carbon matrix as an anode material is an interesting path to improve the specific energy density of Li-ion batteries. However, the volume variation and SEI instability of silicon during cycling should be avoided to obtain stable electrodes. In the present study, silicon nanoparticles (SiNPs) impregnated in a 3D carbon xerogel matrix are synthesized with an ionically-conductive polymer, poly(sodium-4 styrenesulfonate) (PSS), as either a binder or a protective coating. The physico-chemical and electrochemical properties of this novel composite electrode with PSS as a coating or binder improves the retention of reversible capacity by a factor of five as compared to the same electrode using only a conventional poly(vinylidene difluoride) (PVDF) binder. Indeed, the composites with 10 wt.% SiNPs utilizing PSS as a coating or binder retains a specific gravimetric energy density of 450 mAh g⁻¹ composite after 40 cycles. Structural, textural, and electrochemical characteristics as well as prospects for further improvements of this composite anode are discussed.

Keywords: batteries, lithium-ion, anode, silicon, xerogel, poly(sodium 4-styrenesulfonate)

1. Introduction

Lithium-ion (Li-ion) battery technology is an important area of research due to their use in a wide range of applications. Research into this field has focused on improving the energy density, power density, and lifespan of batteries while maintaining safety and minimizing environmental impact. Li-ion batteries store energy by the transfer and storage of electrical charge, *via* Li^+ ions, between two electrodes separated by a separator and an ionically conductive medium. The electrodes are prepared by coating a current collector, usually a copper foil for the anode and an aluminum foil for the cathode, with a slurry containing the electrode ingredients. The slurry is usually composed of the active material, a conductive additive, and a binder dispersed in a suitable solvent. N-methyl-2-pyrrolidone (NMP) or water are commonly used as a solvent depending primarily on the type of binder. NMP is used as a solvent when poly(vinylidene difluoride) (PVDF) is used as the binder whereas water can be used when, for example, carboxymethylcellulose/styrene-butadiene rubber (CMC/SBR) is used as the binder [1-3]. These two polymers are commonly used as a binder in commercial and research applications. Experimental binders, like the electrically conductive copolymer poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) have also been explored due to their unique properties [4,5]. In the current state of the art, intercalation-type materials are most commonly used as the active material, such as graphite for the anode and a lithiated oxide of transition metals, like cobalt, iron, or manganese, for the cathode [6, 7]. In order to improve the energy density of Li-ion batteries, however, alloying-type active materials can be used. Alloying-type materials offer significantly higher energy densities by forming an alloy with lithium instead of

intercalating lithium between atomic layers, thus increasing the number of Li^+ ions stored per atom of active material [8, 9]. Silicon has been shown to be an interesting alloying-type material for a Li-ion battery anode: it exhibits a low electrochemical lithiation and delithiation potential of $<0.35 \text{ V vs. Li}^+/\text{Li}$ and $<0.6 \text{ V vs. Li}^+/\text{Li}$, respectively, and it has a high theoretical energy density of up to 4200 mAh g^{-1} , which is significantly larger than the 350 mAh g^{-1} for conventional graphite [8, 9]. Silicon is also a relatively abundant element in the earth's crust and a large silicon-based economy currently supports the mining and synthesis of high purity silicon metal [10].

Unfortunately, the use of silicon as a Li-ion battery anode has been limited due to instability arising from the large difference in volume (up to 300%) between the lithiated and delithiated states [11]. This difference in volume causes (i) an unstable solid electrolyte inter-phase (SEI) to form and (ii) pulverization of the silicon and the surrounding active material, such as graphite or other conductive additives. [11-13]. Additionally, silicon is a poor electrical conductor, therefore, some type of conductive element is usually required.

Some recent studies have shown positive results which address some of the problems related to silicon as an anode material. Silicon nanoparticles (SiNPs) with a diameter of less than 150 nm have been shown to eliminate or significantly reduce pulverization of the silicon by decreasing the internal stresses caused by the large volume changes; however, the problems of SEI instability and poor electrical conductivity persist [14]. In conventional batteries, the low conductivity transition metal oxides and graphites used as active materials are commonly surrounded with a conductive carbon, like carbon black, which has a relatively low density but gives the electrode a sufficiently high

conductivity [15–18]. These two properties are highly desirable in order to offer both high power density and energy density. However, carbon black can neither act as a support for silicon nanoparticles to accommodate their volume expansion, nor does it protect their surface from SEI instability.

An interesting candidate material for supporting SiNPs could be a carbon xerogel (CX). A CX is an amorphous hard carbon with an interconnected 3D meso-macroporous structure. These meso-macropores are formed by spherical nodules connected in a rigid “string of pearls”-like structure [19]. The CX is prepared *via* a simple and cheap resorcinol-formaldehyde (RF) sol-gel synthesis where the average meso/macro-pore size of the CX can be easily increased or decreased by respectively decreasing or increasing the pH of the precursor solution during synthesis [19]. Additionally, a CX has a nominal intrinsic reversible capacity of approximately 200 mAh g⁻¹, albeit this capacity is achieved *via* a linear lithium insertion/deinsertion potential between 0.005V and 1.5 V vs. Li⁺/Li. [20]. This material should be able to act as a support structure for the SiNPs and offer good electrical conductivity. However, the sole use of this material may not sufficiently mitigate the problem related to SEI instability. An additional protective component could be used as a way to avoid direct contact between the silicon surface and the electrolyte while maintaining ionic conductivity.

Therefore in this work, a composite anode comprised of silicon nanoparticles (SiNPs) supported by a carbon xerogel (CX) is proposed with an ionically conductive polymer, poly(sodium 4-styrenesulfonate) (PSS), as a protective coating or binder to further help mitigate the SEI instability. Electrodes were prepared with (i) PVDF as a binder

(conventional), (ii) PSS as a binder, and (iii) PVDF as a binder with PSS as a coating deposited atop the electrode. These electrodes were electrochemically characterized and compared *via* galvanostatic cycling, electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV). The synthesized CX and CX/SiNPs composites were also physico-chemically characterized with and without a binder to determine pertinent properties of the active material in order to better understand any degradation mechanisms at work during cycling and prevent degradation, if possible.

2. Experimental

Materials: Resorcinol (R, 99%), formaldehyde (F, 37 wt.% in H₂O), sodium carbonate (C, 99.5%), polyvinylpyrrolidone (PVP, $M_w = 40,000 \text{ g mol}^{-1}$), and poly(sodium 4-styrenesulfonate) (PSS, $M_w = 70,000 \text{ g mol}^{-1}$) were purchased from Sigma-Aldrich. Silicon nanoparticles (SiNPs, diameter = 50 nm), poly(vinylidene difluoride) (PVDF), and N-methyl-2-pyrrolidone (NMP, $\geq 99\%$) were purchased from Alfa Aesar.

2.1 Organic xerogel synthesis

An organic xerogel (OX) was synthesized by the polycondensation of resorcinol and formaldehyde with sodium carbonate as a basification agent, following a synthesis method used in previous works [19–22]. The OX was prepared on a molar basis with $R/C = 2000$, $R/F = 0.5$, and a dilution ratio = 5.7 ($D = \text{total solvent/reactants}$) with high purity water (MilliQ, $R > 18 \text{ M}\Omega$) as the solvent. The solution underwent gelation for 3 days at 85°C in a Binder VD-53 oven at atmospheric pressure in a closed synthesis vial. After gelation, the synthesis vial was opened and the solvent was removed by progressively reducing the pressure in the oven every 45 min from atmospheric pressure to 2.5 kPa at 60°C using a

Vacuubrand CVC 3000 pump that was connected to the oven. The pressure was then held at 2.5 kPa for 8 h. After 8 h, the temperature was increased to 150°C while maintaining a pressure of 2500 Pa for 24 h. The OX was then recovered after this drying step as a monolith from the synthesis vial which, due to the removal of the solvent, had undergone approximately a 10% -20% reduction in volume. The sample was then crushed following a method described in a previous work [23] in order to obtain particles with an average size of 10 μm . The monolith was crushed in a crucible and sifted by hand through a 1-mm mesh. The 1 mm powder was ball-milled into a 10 μm OX powder in a Fritsch Pulverisette ball mill at 400 rpm for 60 min. The ball mill consisted of twenty agate balls (diameter = 1 cm) in an agate-lined stainless steel crucible (volume = 80 mL) with approximately 3 g of OX powder per batch.

2.2. Carbon xerogel and carbon xerogel/silicon nanoparticles composites synthesis

Three CX/SiNPs composites were synthesized with 10 wt.%, 15 wt.%, and 30 wt.% of SiNPs. A surfactant, PVP, was dispersed in high purity water (MilliQ, $R > 18\text{M}\Omega$) to a concentration of 20 mg of PVP/mL of H_2O to aid in the suspension of the SiNPs. The SiNPs were then added to the solution with a ratio of surfactant to SiNPs of 10 mg of PVP/mg of SiNP. This suspension was ultrasonicated for 1 h in a Branson 2510 ultrasonic bath to obtain a well-dispersed suspension of the SiNPs. Then the OX was added to the SiNPs/PVP suspension with a mass fraction of silicon to OX of approximately 5 wt.%, 10 wt.%, and 15 wt.% of SiNPs, respectively. These suspensions were also ultrasonicated for an additional 1 h and mixed for 4 h with a magnetic stirrer at 500 rpm at 25°C. The solvent was removed by vacuum filtration through a 0.024 μm PVDF microporous filter. The

collected OX/SiNPs composites were subsequently dried for 24 h at 80°C and 2500 Pa in a vacuum oven.

The three OX/SiNPs composites and the OX without SiNPs were pyrolyzed up to 800°C under a gentle nitrogen flow in a horizontal tubular furnace. Pyrolysis was performed in three successive steps: (i) heating up to 150°C at a rate of 1.7°C min⁻¹, (ii) heating up to 400°C at a rate of 5°C min⁻¹ and (iii) heating up to 800°C at a rate of 5°C min⁻¹. The residence time for each step was 15 min, 60 min and 120 min, respectively. After the last step, samples were left to cool down to room temperature while still under N₂ flow within the furnace. The recovered CX/SiNPs composites were a dark gray color. The recovered CX without SiNPs was black in color. The mass of all four samples had reduced by approximately half, likely due to the conversion of the OX to a CX. The mass fraction of silicon was subsequently confirmed by thermo-gravimetric measurements on a Sensys EVO TG-DSC by heating in air up to 800°C at 2°C min⁻¹ with a residence time of 4.5 h (see Figure S1).

2.3. Preparation of CX and CX/SiNPs inks and electrodes

Three types of electrodes were prepared with the CX without SiNPs and the three CX/SiNPs composites as active material: electrodes with either (i) PVDF as a binder (conventional), (ii) PSS as a binder, or (iii) PVDF as a binder with PSS as a coating deposited atop the electrode were synthesized. The inks with PVDF as a binder were prepared by mixing 90 wt.% of active material and 10 wt.% of PVDF in N-methyl-2-pyrrolidone (NMP, ≥99%, Alfa Aesar) under magnetic stirring at 1000 rpm for 5 h. The inks with PSS as a binder were prepared by mixing 90 wt.% of active material and 10 wt.%

of PSS in high purity water (MilliQ, $R > 18 \text{ M}\Omega$) under magnetic stirring at 1000 rpm for 5 h. A solvent-to-solids mass ratio of 20:1 was used in both cases.

Both types of inks were spray-coated onto pre-weighed 15.5 mm diameter stainless steel disks. Stainless steel disks were used instead of a conventional copper foil in order to accurately measure the mass of the deposited material on each electrode. Stainless steel was confirmed to be stable as a current collector for Li-ion anodes *via* CV measurements on the stainless steel disks with a lithium counter electrode. These disks were fixed on a 70°C heated surface. The coating was performed using a Harder & Steenbeck Evolution Silverline 2 airbrush. A high solvent-to-composite ratio was used to ensure that the prepared inks flowed easily through the airbrush and lead to a homogeneous coating on the stainless steel disks. After spray-coating, the electrodes were dried at 70°C for 2 h at ambient pressure and then at 120°C at 2500 Pa overnight. The electrodes were then weighed to determine the mass of the deposited material prior to their electrochemical characterization. Excess dried material surrounding the electrodes, which was deposited around the disks during the spray-coating process, was collected for further characterization.

For the third type of electrode, a PSS layer was applied to the electrodes synthesized with PVDF as a binder by drop coating a 10 wt.% solution of PSS in high purity water (MilliQ, $R > 18 \text{ M}\Omega$) onto the surface of the spray-coated active layer. Three drops of PSS (1 drop $\approx 50 \mu\text{L}$) were deposited onto the electrode surface. The drop-coated electrodes were subsequently dried once more at 120°C at 2500 Pa overnight. Approximately 15 wt.%

of PSS with respect to the amount of spray-coated active material was deposited, measured via a mass balance before and after the PSS coating procedure.

2.4. Physico-chemical characterization

The pore size distribution of the CX powder without any SiNPs or binder was measured by mercury porosimetry on a Thermo-Scientific Pascal 140/240. Measurements were performed between 0.01 MPa and 200 MPa. The mercury intrusion data obtained were analyzed to determine the size distribution of pores larger than 7.5 nm in diameter as well as the CX powder particle size. The average pore size, d_{pore} , was calculated by using the Washburn equation, shown below in Equation 1:

$$d_{\text{pore}}(nm) = -\frac{4\gamma\cos(\theta)}{P_{Hg}} \approx \frac{1500}{P_{Hg}} \quad (1)$$

where P_{Hg} is the mercury pressure (MPa), γ is the surface tension of mercury ($m\text{ Nm}^{-1}$), and θ is the contact angle between mercury and the carbon at 20°C [24]. The surface tension of mercury and the contact angle between mercury and carbon are 485 mN m^{-1} and 152.5° , respectively [25, 26]. The CX powder particle size can be estimated by assuming that the sample is represented by a hexagonal compact packing of ideal spherical particles. In this case, the volume between the ideal spheres is able to contain a theoretical volume seven times smaller than the diameter of the constituent ideal spheres. Since this central void volume is the volume probed by mercury porosimetry, the following alteration to the Washburn equation estimates the particle diameter, d_{particle} , of the CX [23, 27]:

$$d_{\text{particle}}(nm) = \frac{1500}{P_{Hg}} \quad (2)$$

The CX/SiNPs composites with and without a binder were characterized by nitrogen adsorption-desorption analysis at -196°C on a Micromeritics ASAP 2420 instrument. Prior to measurements, the samples were degassed overnight at 270°C under vacuum (133 Pa). The adsorption-desorption characterization yields the following quantities: (i) the total specific surface area (S_{BET}), which was calculated by applying the Brunauer-Emmett-Teller theory to the adsorption data obtained in the relative pressure range from 0.01 to 0.10 [28], (ii) the micropore surface area (S_{micro}), which is the cumulative surface area of all pores with a diameter less than 2 nm, and (iii) the external surface area (S_{ext}), *i.e.* the cumulative surface area of all pores with a diameter greater than 2 nm, which corresponds to the mesopores of the CX (2-50 nm) and any other surface areas of the CX particles. S_{micro} and S_{ext} were calculated *via* the t-plot method. The sum of S_{micro} and S_{ext} should approximately equal S_{BET} .

TEM micrographs of the CX without SiNPs, CX/SiNPs composites, and the as-received SiNPs were obtained using a Philips CM100 TEM operating at 80 kV. The CX, CX/SiNPs composite, and SiNPs were deposited onto Agar Scientific 200 mesh copper micro-grids covered with a PVDF film. The copper micro-grids were dipped into a dilute dispersion of each sample in ethanol (1 mg mL^{-1}). The copper micro-grids were subsequently dried in ambient conditions for at least 1 h before being introduced into the microscope.

SEM imaging was obtained on the stainless steel electrodes coated with a CX and CX/SiNPs composites using a Philips ESEM-XL30 at 7.5 kV under high vacuum. The samples were prepared by gently placing the electrodes against a small piece of glass slide

that had been coated with a double-sided conductive carbon tape. The glass slide was then stuck on its edge with the same carbon tape to the SEM sample holder so that that edge of the electrode was facing perpendicular to the surface of the SEM sample holder.

2.5. Electrochemical Half-Cell Preparation

Half-cells of the CX and CX/SiNPs composite electrodes were assembled in CR2032 coin-cells with a lithium metal foil as the counter-electrode (Li-metal, MTI Corporation). In this half-cell configuration, the insertion of Li^+ ions inside the composite structure corresponds to a decrease in potential, whereas the de-insertion corresponds to an increase in potential. This setup is opposite to that of a full-cell, where the CX/SiNPs composite would be the negative electrode and a metal oxide, such as LiCoO_2 for instance, would be the positive electrode. Two porous polyethylene separators (Celgard, 25 μm thickness, MTI Corporation) soaked with 80 μL of electrolyte (1 M LiPF_6 in a 1:1:1 ratio of ethylene carbonate: diethylene carbonate: dimethyl carbonate, Selectilyte LP71, Merck) were placed between the Li-metal disk and the CX/SiNPs electrode. The half-cells were assembled in an Argon-filled glovebox (MBraun MB200B).

2.6. Electrochemical Characterization

All electrochemical measurements were conducted on the assembled half-cells. At least two coin-cells of each formulation were characterized under identical conditions of each formulation in order to ensure the reproducibility of the results. Galvanostatic cycling was recorded using a Neware BST8-WA, 8 channel Battery Analyzer at a rate of approximately C/10 (by considering the theoretical capacity for carbon and silicon and the respective mass percent for each formulation) between 0.005 V and 1.5 V vs. Li^+/Li . The coin-cells were kept inside a climate controlled chamber at 25°C to ensure temperature stability. EIS

measurements were conducted using a Biologic VMP3 multichannel potentiostat on each sample between 1 MHz and 10 mHz with a voltage amplitude of 10 mV and 10 data points per decade on the pristine half-cell, and after the 1st, 5th, 20th, and 50th cycles. The measurements were recorded in the delithiated state (*i.e.* the high potential, charged state). CV measurements were performed using a Biologic VMP3 multichannel potentiostat on each sample over a potential window of 0.005 V to 3 V vs. Li⁺/Li at a scan rate of 0.05 mV s⁻¹ for the first five cycles.

2. Results

2.1. Textural characterization of the CX and CX/SiNPs composites

Mercury porosimetry was conducted on the as-synthesized CX without SiNPs in order to determine the particle size and pore size distribution of the CX support matrix. In Figure 1, the two inflection points at 1 MPa and 11 MPa correspond to the intergranular volume of the powder and meso/macro-porosity volume of the CX particles, respectively. The average powder particle size, d_{particle} , was calculated to be $\approx 10\mu\text{m}$ using Equation 2 at the 1 MPa inflection point. The average pore size, d_{pore} , was calculated to be $\approx 120\text{ nm}$ using Equation 1 at the 11 MPa inflection point. The pore size distribution was also calculated and is displayed in Figure S2. The pore size distribution ranges from approximately 10 nm to over 200 nm with a full width half max (FWHM) of 50 nm. The average pore diameter of 120 nm seems sufficiently large to support the SiNPs; however the wide pore size distribution could possibly affect the electrochemical characteristics of the xerogel as well as the ability of the material to act as a host matrix for the dopant silicon.

In order to further understand the interaction of the binder with the CX, nitrogen adsorption-desorption analysis was performed on: (i) the pristine CX material, (ii) the CX with PVDF as a binder, and (iii) the CX with PSS as a binder. The latter two were recovered from the electrode processing by scratching the material from the surface surrounding the electrodes. Corresponding N₂ isotherms are shown of these three materials in Figure 2. The CX without a binder resembles a type I/II isotherm, corresponding to a material that includes micropores as well as a distribution of largeness-macropores, which agrees with the results obtained from Hg porosimetry. Interestingly, the CX with either PSS or PVDF as a binder shows a decrease in the adsorbed quantity of nitrogen at low relative pressure (*i.e.* before the plateau in Figure 2), which corresponds to a decrease in the micropore surface area. The reduction of micropore surface area is greater for the CX with PVDF as a binder as compared to the CX with PSS as a binder. The inaccessibility of the micropore surface area during this analysis is an indication that these surfaces would also be inaccessible to the electrolyte in the half-cell configuration [19, 22].

The actual morphology of the CX with either binder remains an open question. For the CX with PVDF as a binder, given that the micropores surface area is completely lost, the possible morphologies must be that either (i) the PVDF completely fills the micropores or (ii) the PVDF homogeneously covers all the micropores. As for the CX with PSS as a binder, since the micropore surface area is not completely lost, possible morphologies must include either that (i) the PSS partially fills the volume of micropores, (ii) the PSS heterogeneously covers some micropores that leaves an interior micropore surface that is not measurable by N₂ adsorption, or (iii) the PSS adheres to the micropore surfaces to some

extent but does not fill the volume of the micropores (see Figure 3). These configurations depend on several parameters, such as the wettability of the CX, the nature of the binder, and the size of the solvent molecules and binder oligomers. As an example, the surface hydroxyl groups usually present on the CX surface should give the CX a more hydrophilic nature, which would help aid the wetting of the micropore surfaces given the solvent is water [19, 29]. It was indeed previously suggested that water could enter the small pores of the CX structure more easily than NMP, which would help the binder to enter the micropores as well [20]. However, no exact mapping of the binder location could be achieved to date.

Nevertheless, it is possible to partially discriminate between the aforementioned configurations. In order to rule out the possibility that either binder is just filling in the micropores rather than covering the micropores, a calculation was performed of the respective amounts of micropore volume in the CX and volume of binder applied. The available micropore volume of the CX powder was found to be approximately 2 and 5 times larger than the volume of PSS or PVDF available during the synthesis, respectively (Table 1). Additionally, the topographical polar surface area (TPSA), which is a measure of the physical size of any given molecule, shows that the NMP solvent molecule, with a $TPSA = 20 \text{ \AA}^2$, is much larger than the water molecule ($TPSA = 1 \text{ \AA}^2$) [30, 31]. Therefore, PVDF dispersed in NMP should not infiltrate the micropores as easily compared to the PSS in water, especially given that these pores have a maximum pore diameter of 2 nm (surface area = $300 \text{ \AA}^2$). As a result, the PVDF should be located mainly on the external surface area of the microporous carbon nodules, *i.e.* at the meso/macro-pore surface of the CX, rather

than depositing inside the micropores. On the contrary, the likely hydrophilic nature of the CX and physical size of the water molecule would facilitate the ability of the PSS to infiltrate into the confined volume of the micropores. If one assumes that PSS does not completely fill some micropores while others are left empty, the most probable morphology for the PSS on the CX should be that the PSS is able to partially enter all the micropores homogeneously and retain some of the internal surface. Nevertheless, it cannot be said with certainty that these proposed morphologies are correct.

2.2. TEM and SEM Micrographs

TEM micrographs were taken of a CX without a binder, SiNPs, and the CX/SiNPs composite with 15 wt.% SiNPs and no binder. The CX/SiNPs composite shown is given as an example since all the CX/SiNPs composites had similar morphologies. Figure 4a shows the xerogel support without SiNPs with the typical “string-of-pearl”-like structure. The structure is composed of a cluster of spherical nodules linked together that forms a meso/macro-porous material [19, 20, 23]. Although the CX has microporosity, as confirmed by the N_2 analysis, these micropores located in the nodules are not identifiable in these images given their small size. Figure 4b shows SiNPs as-received from the supplier. The SiNPs surprisingly have the same “string-of-pearl”-like morphology, similar to that of the CX. The aggregation of the particles into long chains forms a much larger macrostructure on the order of hundreds of nanometers, even though the average diameter quoted by the supplier was less than 50 nm. However as shown in Figure 4c, after suspension and impregnation into the xerogel support, the aggregation of the SiNPs seemed to decrease, possibly due to the loss of the larger SiNPs aggregates during filtration that did not adhere to the CX, the extensive ultrasonication of the SiNPs during the composite

synthesis, or the pyrolysis step. The larger SiNPs seem to also aggregate around the outside of the CX particles while the smaller SiNPs have the ability to infiltrate further into the CX possibly as a result of the size of the CX meso/macropores. Apart from the difference in size and shape between the SiNPs and CX, dark field images and EDX analysis were used to further discriminate between the CX and silicon phases (Figure S3 and S4). A particle size distribution was determined by manually measuring the diameter of individual SiNPs and is shown in Figure S5a with the corresponding TEM micrograph in Figure S5b. The number average diameter of the SiNPs in the CX/SiNPs composite was determined to be approximately 51 nm.

Figure S6 shows SEM micrographs of the active material layer of CX/SiNPs composite with 15 wt.% SiNPs deposited on stainless steel disk with PVDF as a binder (Figure S6a) or PSS as a binder (Figure S6b). These CX/SiNPs composite are given as an example since all the other CX/SiNPs composites had similar morphologies. The CX/SiNPs composite particles seem to be less densely packed with PVDF as a binders compared to with PSS as a binder. The density of the active layer with PVDF as a binder and PSS as a binder was calculated to be approximately 42.5 mg cm^{-3} and 60.6 mg cm^{-3} , respectively. The density of the active layers were calculated given the mass of the deposited CX/SiNPs composite, the surface area of the current collector, and the thickness of the active layer observed *via* SEM.

2.3. Cyclic Voltammetry

CV measurements were conducted on CX and CX/SiNPs composite electrodes with PVDF as a binder and 15 wt.% SiNPs (Figure S7). Similar results were obtained with the anodes

synthesized with PSS as a binder or PSS as a coating as well as with 10wt.% and 30 wt.% of silicon. The CV measurements for the 1st and 5th cycles are shown; the 2nd, 3rd, and 4th cycles are similar to the 5th cycle. In Figure S7a, the first cycle of the undoped CX shows three peaks at 1.3 V, 0.6 V, and ≈ 0 V vs. Li⁺/Li. The reduction peaks during the first cycle at 1.3 V and 0.6 V vs. Li⁺/Li may be attributed to either SEI formation or possibly the trapping of Li⁺ ions within the carbon xerogel. SEI layers on carbon materials have been shown to form due to the instability of the electrolyte below approximately 1.3 V vs. Li⁺/Li [32–34]. The underlying peak that spans along the entire voltage window during lithiation, reaching a minimum around 0 V vs. Li⁺/Li, likely corresponds to the insertion of lithium into the CX [19, 20, 23, 35]. The wide insertion window may be attributed to both the mesoporous structure of CX as well as the amorphous hard-carbon nature of the graphitic layers in the CX, as supported by previous studies [19, 20, 23]. This is contrary to conventional graphitic anodes that have a narrow insertion and de-insertion potential as a result of the regular spacing between graphitic layers. In Figure S7a, the disappearance of the two lithiation peaks after the first cycle indicates the formation of a stable SEI.

Figure S7b shows the CV measurements obtained using a CX/SiNPs composite anode doped with 15 wt.% SiNPs with PVDF as binder. The 1st cycle discharge exhibits similar peaks at 0.6 V vs. Li⁺/Li related to SEI formation on the CX (peak1). However, an additional strong lithiation peak below 0.1 V vs. Li⁺/Li (peak 2) is likely related to the initial alloying of crystalline silicon with lithium and SEI formation between the silicon and electrolyte. It is difficult to differentiate between these two phenomena. However, previous studies have come to similar conclusions regarding the initial electrochemical silicon-

lithium alloying peaks. [32–37]. During the 1st delithiation, reduction peaks at 0.3 V to 0.6 V vs. Li⁺/Li relate to the de-alloying of lithium from silicon (peak 3) [37]. During the 5th cycle, similar de-alloying peaks are observed; however, an alloying peak appears at 0.2 V vs. Li⁺/Li, which has been attributed to the lithiation of amorphous silicon (peak 4) [38–40].

2.4. Galvanostatic Cycling

Galvanostatic cycling was conducted on the CX without SiNPs and all three CX/SiNPs composites (10 wt.%, 15 wt.%, 30 wt.% SiNPs) with either PVDF as a binder, PSS as a binder, or PVDF as a binder with PSS as a coating. Indeed, CX/SiNPs composites with PVDF as a binder exhibited poor capacity retention. A CX/SiNPs composite with 10 wt.% SiNPs and PVDF as a binder is shown in Figure 5a as the solid line, which retained 80 % of the 1st cycle capacity after only 6 cycles. However, the reversible capacity retention of the same CX/SiNPs composite with either PSS as a binder or PSS as a coating reached 40 cycles before the reversible capacity dropped below 80% of the 1st cycle capacity. Similar cycle stability results were obtained for the CX/SiNPs composites with 15 wt.% and 30 wt.% SiNPs, which are not shown.

Figure 5b shows a comparison between CX/SiNPs composites with PVDF as a binder with PSS as a coating with 0 wt.%, 10 wt.%, 15 wt.%, and 30 wt.% of SiNPs. As the weight percent of SiNPs is increased, the initial specific capacity increases accordingly; however, sharp decreases in the capacity are observed for the first few cycles for composites with 15 wt.% and 30 wt.% of SiNPs (Figure 5b). After this initial sharp decrease in reversible capacity, these CX/SiNPs composites tend to follow a similar loss of capacity per cycle as the 10 wt.% silicon CX/SiNPs composite.

2.5 Electrochemical Impedance Spectroscopy

EIS responses for CX/SiNPs composite anodes with 15 wt.% SiNPs with either PVDF as a binder (Figure 6a), and PSS as a binder (Figure 6b), and PVDF as a binder with PSS as a coating (Figure 6c) have been collected. Similar results were obtained with CX/SiNPs composites with 10 wt.% and 30 wt.% SiNPs. A simplified Randles cell was used as a model for this system. The features of interest are the intercept of the curve with the real axis (abscissa) at high frequency and the diameter and position along the abscissa of the prominent half circle. The abscissa intercept has been shown to represent the equivalent series resistance of the electrolyte and electrodes. The diameter of the half circle can be considered as a representation of the charge transfer resistance (CTR) between CX/SiNPs composite anode and the electrolyte [25]. Likewise, the position of the half circle along the abscissa can be used to calculate a charge transfer capacitance (CTC) at this interface. Given the CTC and CTR, a characteristic time can be calculated, which, in other words, represents the speed at which charge transfer of Li^+ ions across this interface occurs [26, 27]. In general, half circles with a large diameter and with a center located at a higher real impedance correspond to slower kinetics of a given reaction in the electrochemical half-cell.

The CTR of the pristine half-cells (before cycling) are higher for the CX/SiNPs composites that have PSS as a binder or coating as compared to composites with PVDF as a binder, given that the diameter of the half-circles are smaller for the PSS-based composites as compared to the PVDF-based composites (Figure 6). The diameter of the half-circle decreases for all the CX/SiNPs composites between the pristine half-cells and the 1st cycle. This can be related to a lower CTR likely due to the mechanical stability and

ionically-conductive nature of the SEI. A progressive increase in the diameter of the CTR half-circle is observed between the 1st and 50th cycle for the composites with PVDF as a binder (Figure 6a). Contrarily, a decrease in the diameter of the CTR half-circle is observed for the first 20 cycles of the composite with PSS as a binder (Figure 6b) and PSS as a coating with a PVDF binder (Figure 6c). However, a dramatic increase of the diameter of the CTR half circle at 50 cycles is observed for the composite with PSS as a binder. Likewise, the 50th cycle for the composites with PSS as a coating shows an irregular response at lower frequencies. A second half circle at or after the 50th cycle is observed at high frequency for all three types of the CX/SiNPs composites, most likely due to the excessive buildup of SEI, which possibly forms a secondary kinetically-limited layer.

3. Discussion

Improved stability of the reversible capacity of CX/SiNPs composite anodes with PSS as binder or PSS as a coating as compared to an anode with PVDF as a binder has been observed. The improved cycle stability may be due to the ionic conductivity of the PSS and improved interface properties between the PSS and the CX/SiNPs composite. *Note that, for comparison, electrodes without CX (i.e. SiNPs with PSS as binder - with 20 wt.% PSS and 80 wt.% SiNPs) were prepared and characterized using EIS measurements, CV, and the start of galvanostatic cycling measurements. Results show that Si could be fully lithiated and delithiated after a few cycles, but only at extremely low cycling rate. This comes from the very high electrical resistance of the electrode (about 3 to 4 Ω). This clearly indicates that the carbon support is necessary for electron conductivity of the system. However, composites that included PSS as a binder or coating still only exhibited a rather short period*

of stable reversible capacity followed by a gradual loss of capacity. This phenomenon may be due to the loss of PSS into the electrolyte, which would have two effects on the impedance of the half-cell: (i) a constant increase in the electrolyte resistance caused by the poisoning of the electrolyte with PSS and (ii) a decrease in charge transfer resistance (CTR) that reaches a minimum as the layer of PSS becomes thinner followed by an increase of the CTR as the SiNPs pulverize and form an unstable SEI. Interestingly, there is evidence for this model if one considers the EIS measurements presented in Figure 6b, where PSS is used as a binder. The CTR half circles are shown to be decreasing in diameter, corresponding to faster charge transfer of Li^+ ions into the active material up until 20 cycles. Then an increase in the CTR diameter is observed between 20 and 50 cycles; this could correspond to an unstable SEI layer which leads to an excessive buildup of SEI, which consumes electrolyte. Likewise, a gradual increase in electrolyte resistance is observed during the entire duration of the cycling, which may correspond to the poisoning of the electrolyte by PSS and the loss of electrolyte to SEI formation. Figure 7 displays the CTR and electrolyte resistance together and a possible corresponding morphology of the SiNPs and the SEI layer for each regime.

A possible cause for the better cycling stability for CX/SiNPs composites with PSS as a binder or PSS as a coating may also be due to a difference in the morphology of the active layer as compared to the composites with PVDF as a binder. The change in the active layer morphology could be explained by considering how each respective binder covers the available surfaces of the CX. Previous studies as well as this work have shown that it is likely that PVDF preferentially deposits on the meso/macro-pore surface of the active material [41, 42]. This observation is supported in this work by the N_2

adsorption/desorption analysis showing how the PVDF covers the micropores and only deposits on the surface outside of the carbon nodules, *i.e.* S_{ext} of the CX. The morphology between the CX and PSS proposed in this work was that the PSS likely enters the micropores of the CX to some extent, due to the properties of the solvent and binder and the surface chemistry of the CX. High resolution TEM micrographs were recorded of the CX/SiNPs composite with 20 wt.% SiNPs to try and identify the location of the PSS, however, the low electron density of the polymer makes the imaging difficult (see Figure S8). As a consequence of these different morphologies, the active layers with PVDF as a binder was observed to be less dense than the active layers with PSS as a binder. A proposed reason for this effect is that the PVDF forms thick, bridge-like connections between particles while the PSS forms a thinner, point-like connection between particles. If true, PVDF would therefore act as a better binder since there is more PVDF available to mechanically bind particles to each other, *via* bridges on their external surface, and less so for PSS since more of the PSS is used to coat the micropore surfaces. However, PSS would arguably be a better protective material due to its better contact between surfaces on the active material, better structural integrity of the active layer due to the higher density, and its ionically conductive nature.

4. Conclusion

Carbon xerogel and SiNPs composite anodes were synthesized with an ionically conductive polymer as either a protective coating or binder. CX/SiNPs composites with 0 wt.%, 10 wt.%, 15 wt.%, and 30 wt.% SiNPs were synthesized with PSS as a binder or coating and compared to the same CX/SiNPs composites synthesized with PVDF as a binder. The

reversible capacity retention of CX/SiNPs composite anodes were improved when either PSS as a coating or PSS as a binder was used rather than only PVDF as a binder. The CX/SiNPs composite anodes with either PSS as a coating or PSS as a binder reached 80% the initial capacity after ~40 cycles while the composite anodes with PVDF as a binder reached 80% the initial capacity after only 6 cycles. However, sharp decreases in the capacity were observed for the first few cycles for composites with higher weight fractions of silicon (15 wt.% and 30 wt.%). These CX/SiNPs composites with high weight fractions of silicon tended to follow a similar loss of capacity as the low weight fraction of silicon composites after this initial sharp decrease during the first 5 cycles.

Although the morphology of the PSS on the active material is not definitively known, a likely candidate has been determined. Further characterization to determine the true morphology of the electrode, *i.e.* the nature of the contacts between all elements, would be necessary in a further study; however, since these characterizations are quite heavy to perform, the first logical step would be to first improve the system in order to highlight the relationship between the electrode morphology and its performance in the battery. However, considering the proposed morphology of the PSS on the surface of the CX/SiNPs composites is close to correct, this morphology as well as a denser and more adhered active layer may have helped protect the active material from breaking apart and ensure ionic and electronic conductivity throughout the active layer.

Impedance measurements indicated that a loss of PSS into the electrolyte may be the cause of the cycle instability of these composites. Further study into PSS as a protective layer may be focused on reducing the brittleness of PSS by cross-linking, using elastic co-

polymers, or functionalization of the PSS, which would help maintain adhesion of the protective layer to the silicon and carbon support. The characterization of the SEI and its modification with time in the case of the proposed CX/SiNPs with PSS as a binder remains a key point to the understanding of such electrodes. If the system can be improved further, the SEI evolution should thus be carefully studied; this will be considered in further studies. Additionally, apart from a carbon xerogel, we could envision other carbon structures as a support for SiNPs, such as carbons obtained by templating, nanotubes, nanofibers, graphene, or other morphologies that can be more finely controlled.

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6. Tables

Table 1: N₂ adsorption data for CX powder without a binder, with PSS, or with PVDF as binder.

Sample	S_{BET} (m ² g ⁻¹)	S_{ext} (m ² g ⁻¹)	S_{micro} (m ² g ⁻¹)	$V_{\text{DUB}}^{\text{a}}$ (cm ³)	$V_{\text{binder}}^{\text{b}}$ (cm ³)
CX powder	653	154	499	0.052	- ^c
CX + PVDF	87	77	10	- ^d	0.011
CX + PSS	399	87	312	- ^d	0.025

^aCalculated *via* the Dubinin-Radushkevich method and given the mass of CX powder used during synthesis. ^bCalculated given $v_{\text{PVDF}} = 0.56 \text{ cm}^3 \text{ g}^{-1}$, $v_{\text{PSS}} = 1.25 \text{ cm}^3 \text{ g}^{-1}$, and the mass of binder used during synthesis. ^cNot relevant. ^dNot calculated. V_{binder} should be compared to V_{DUB} of the CX powder.

7. Figures

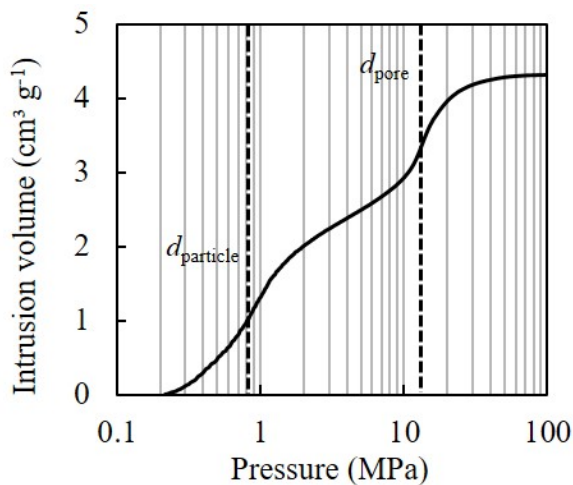


Figure 1: Hg Intrusion volume as a function of the applied Hg pressure of the synthesized CX powder without a binder. The inflection points labeled by the dotted lines at approximately 1 MPa and 11 MPa can be used to calculate the average particle size, d_{particle} , and average pore size, d_{pore} , respectively.

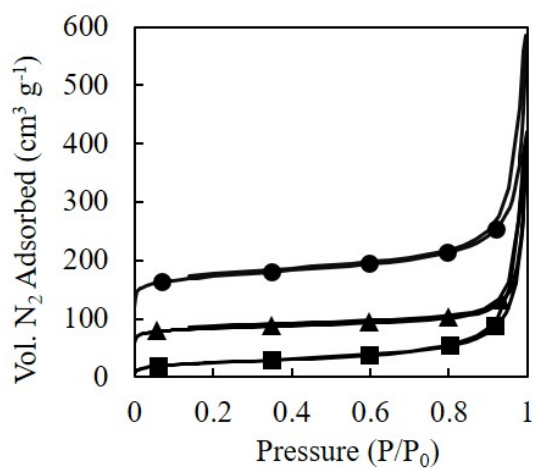


Figure 2: Nitrogen adsorption isotherms for the undoped CX powder without a binder (●), with PSS as binder (▲), and with PVDF as binder (■).

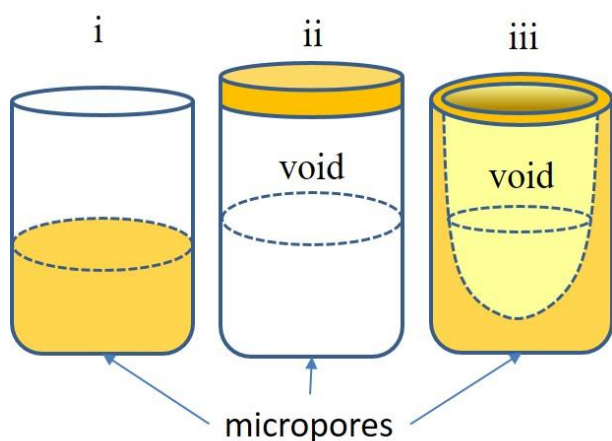


Figure 3: Representation of possible morphologies of the PSS binder within a cylindrical micropore. (i) The PSS partially fills the volume of micropores, (ii) the PSS covers some micropores, leaving an internal void volume, or (iii) the PSS adheres to the micropore surfaces to some extent but does not fill the volume of the micropores. The internal surfaces are indicated by the dotted lines.

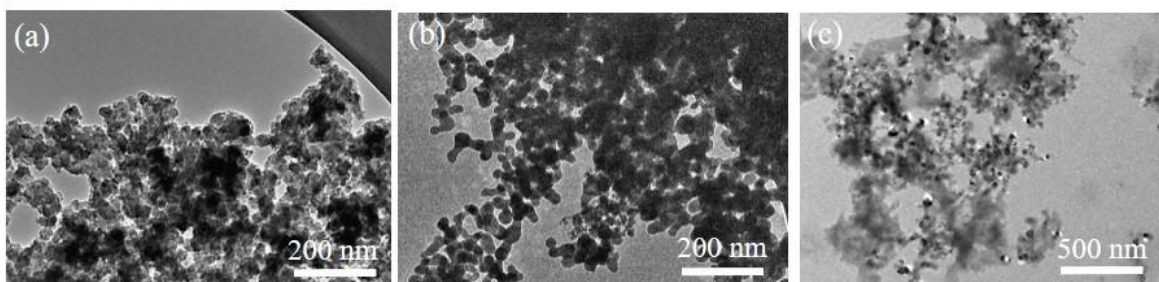


Figure 4: (a) Carbon xerogel, (b) as-received commercial silicon nanoparticles, (c) carbon xerogel and 15 wt.% silicon nanoparticles composite.

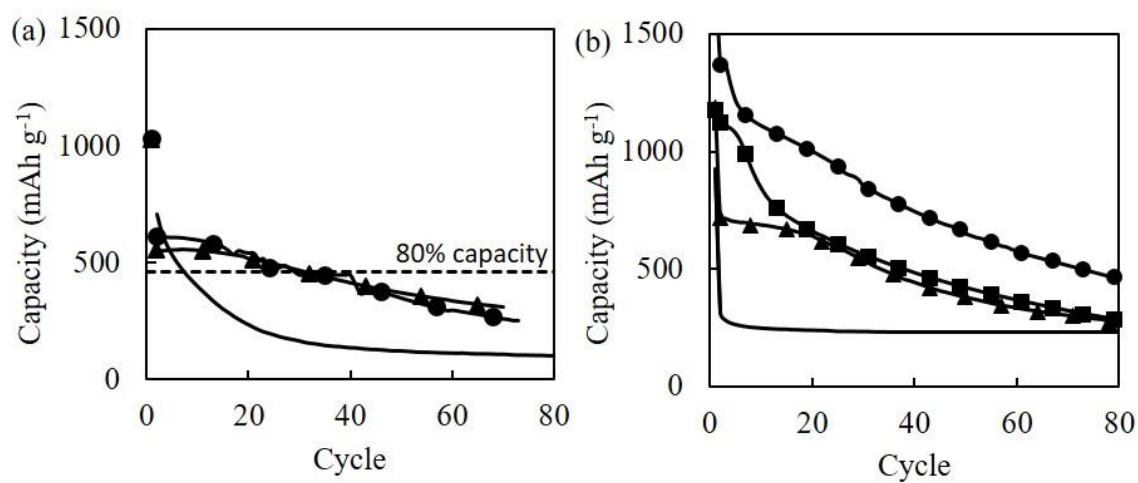


Figure 5: (a) Galvanostatic cycling of CX/SiNPs composite with 10 wt.% SiNPs using PVDF as a binder (—), PSS as a binder only (▲), or PVDF as a binder with PSS as a coating (●). (b) Galvanostatic cycling of CX/SiNPs composites with 0 wt.% (—), 10 wt.% (▲), 15 wt.% (■), and 30 wt.% (●) silicon with PVDF as a binder and PSS as a coating.

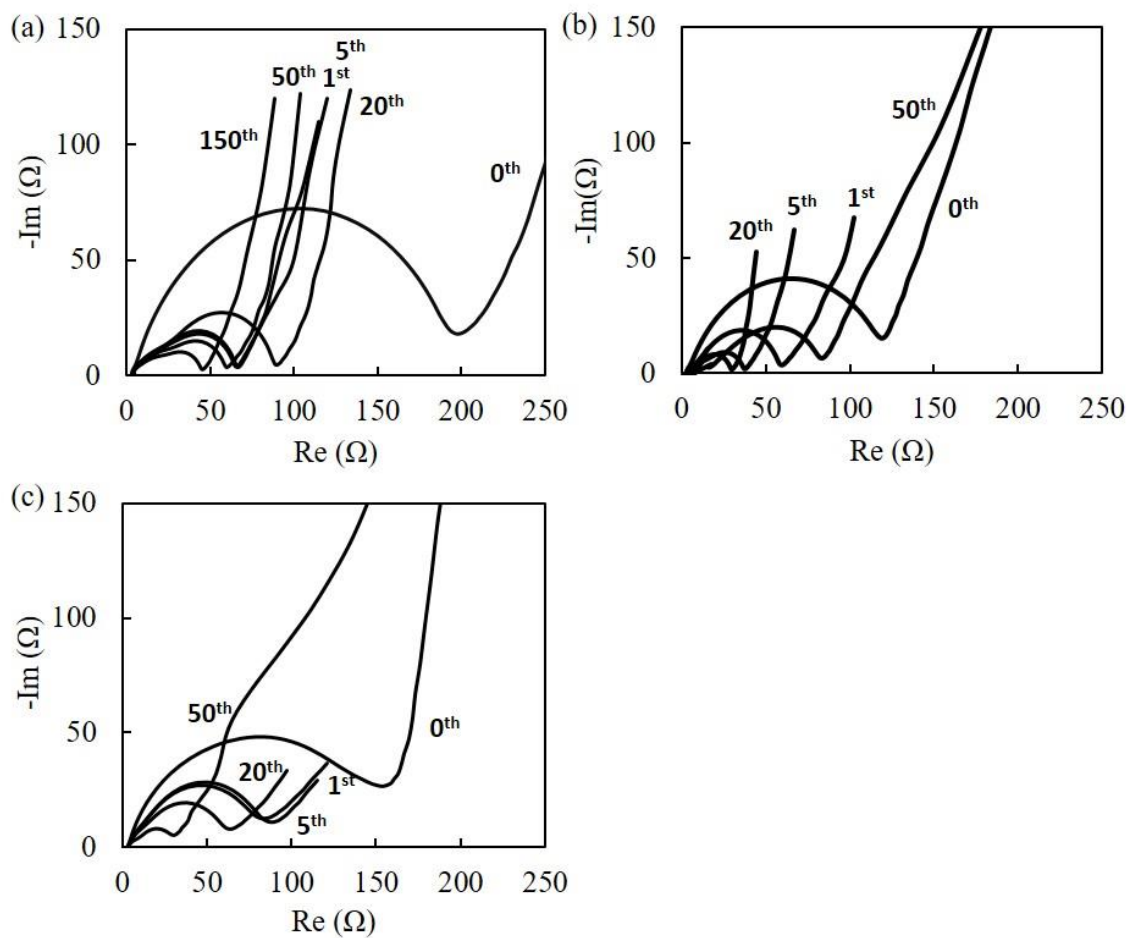


Figure 6: Electrochemical impedance spectroscopy of 15 wt.% CX/SiNPs composite with (a) PVDF as a binder, (b) PSS as a binder, and (c) PVDF as a binder and PSS as a coating, Each curve is labeled with the respective cycle at which the measurement was recorded.

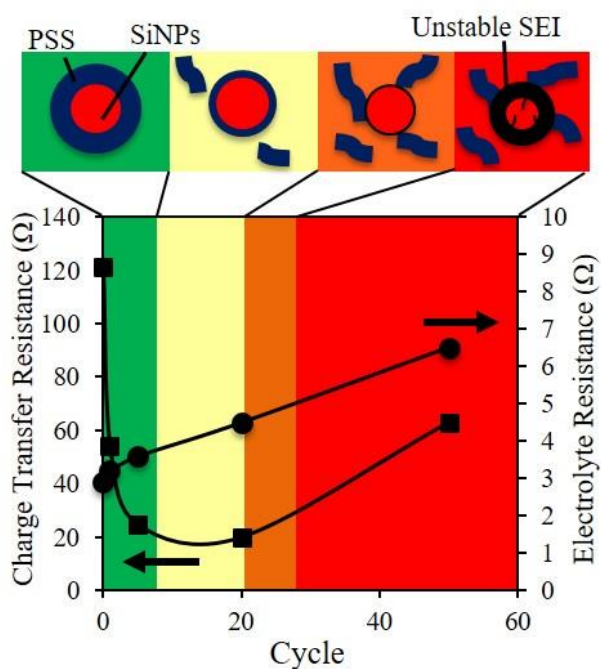


Figure 7: Charge transfer resistance (■) and electrolyte resistance (●) vs. cycle number for a CX/SiNPs composite with PSS as a binder. Values for CTR and electrolyte resistance were calculated by considering the half circle diameter and abscissa intercept at high frequency, respectively, for the EIS measurement shown in Figure 6c. A proposed schematic representation of PSS dispersion and SEI instability on the SiNPs are shown below the figure. The yellow outline and fragments represent the PSS dispersing into the electrolyte. The thickening black outline represents the excessive SEI formation on the silicon nanoparticle surface after PSS has broken away.