



# Improving cycle stability of Si anode through partially carbonized polydopamine coating

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## ABSTRACT

In this study, we report the first investigation of the effectiveness of the partially converted carbon coating from polydopamine (PDA) to improve the cycle stability of Si anode for Li-ion batteries. It is hypothesized that by converting PDA to a partial carbonization condition, the resulting coating could have a higher electrical conductivity than PDA without carbonization, and at the same time may still contain some organic bonds and thus mechanical flexibility to accommodate the volume expansion of Si during lithiation. The results show that such a partial carbonization state can be obtained by carbonization of PDA at 400 °C. Furthermore, the partially converted carbon coating can offer sufficient electrical conductivity for lithiation and delithiation of Si anode while drastically reducing the charge transfer resistance for the redox reactions. In addition, the partially-converted-carbon coated hollow Si nanospheres exhibit excellent cycle stability when the volume expansion of Si anode is not very large (~88%) even though this volume expansion is significantly larger than the engineered void space (47% of the Si volume) available inside the partially-converted-carbon coated hollow Si nanospheres, unambiguously confirming the good tolerance of the partially converted carbon coating in withstanding some tensile strain without fracture. This study offers a new direction for systematic studies in the future as a means to provide a coating on Si material with sufficient electrical conductivity along with capability to withstand some tensile strain during the volume expansion of Si, thereby improving the cycle stability of Si anodes.

## 1. Introduction

Hollow core/shell nanoparticles have attracted huge attention in various fields including semiconductor, catalyst, separation, nanomedicine, pigments, energy storage, gas adsorbents, biotechnology, and etc. [1–10]. This is due to the outstanding properties derived from this nanostructure. The nanoscale size of this family of nanomaterials leads to higher mechanical properties, increased specific surface area, and increased surface reactions compared to the bulk reactions. Thus, utilizing this class of nanomaterials is extremely favorable to augment the electrochemical reaction rate of alloying anode materials for Li-/Na-ion batteries such as Si and Sn, which typically exhibit sluggish electrochemical reaction. Furthermore, with the aid of fine chemistry methods, the size, shape, morphology, inter-space and number of shells can be tuned in the nanostructure [11–16].

Silicon with its high abundancy and theoretical specific capacity of 3590 mA h g<sup>-1</sup> at room temperature, which is almost 10 times the specific capacity of the current graphite material, has been studied as anode material for more than 15 years [17–24]. However, the current status of silicon anodes is not satisfying. This is because of its intrinsic low electrical conductivity and huge volume change during lithiation [6,19–24]. To overcome the problems, many strategies have been attempted including downsizing

micron size silicon to nanoscale, dispersing silicon in conductive matrix, designing core/shell and yolk/shell nanostructured silicon, coating with different conductive elements, developing multifunctional binders, and adding new electrolytes additives [6,17–25]. Considering all of the improvements mentioned above, it looks that a multi-aspect approach is required to introduce a high performance silicon-based anode. The hollow core/shell or yolk/shell silicon nanoparticles [26–37] are interesting since their high specific surface and high porosity act as fast highways for Li<sup>+</sup> ions and electrons transfer, while silicon has sufficient space to expand inward with a stable solid-electrolyte interface (SEI) formed outside of the nanoparticles. Furthermore, the low conductivity of silicon can be resolved by applying a thin conductive coating such as copper, silver and carbon [26–37]. However, the synthesis of such fine hollow nanomaterials is challenging. The key to success is to maintain the electrical contact between the particles, while minimizing the strains associated with expansion of silicon. Thus, the shell(s) materials and thickness are extremely important. The carbon is among the best materials for the shell since the carbon sources are not expensive and carbon coating has been performed by industries for many years. The carbon should be deposited uniformly on the surface of the material and carbonization of carbon precursors should be performed under inert atmosphere as well as at higher temperatures, if possible, to

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achieve more graphitized carbon layer with higher electronic conductivity. The carbon coating improves the electronic conductivity and could serve as mechanical restraint to make silicon expand inward [6,32,35]. The carbon coating layer can be derived from chemical vapor deposition (CVD) or polymerization/carbonization of polymers including polyaniline (PANI), polyacrylonitrile (PAN), polypyrrole (PPy), polydopamine (PDA), phenolic resins, etc. [29,30,34,36–39]. Dopamine can self-polymerize in mild basic solution and cover the surfaces of different materials uniformly. It contains many amine groups in its structure and therefore, after carbonization, the carbon layer is doped with nitrogen and having good electrical conductivity [40–43]. The typical carbonization temperature for PDA is from 700 to 900 °C to achieve good electrical conductivity [29,30,34,42]. Interestingly, PDA coating is also used directly without carbonization [44]. In this case, the imino groups of PDA react with carboxyl groups to cross link polyacrylic acid (PAA) binder, thus serving as a bridge to bind Si particles to the PAA binder strongly and suppressing the Si particle pulverization [44]. Using this strategy, Si nanoparticles coated with PDA coating have indeed been demonstrated to have better cycle stability than the counterparts without PDA coating.

Inspired by the aforementioned studies of PDA coatings in use with and without carbonization [29,30,34,40,42,44], here we aim to investigate the feasibility of converting PDA to a partial carbonization condition which could have a higher electrical conductivity than PDA without carbonization, but at the same time may still contain some organic bonds and thus mechanical flexibility to accommodate the volume expansion of Si during lithiation. If successful, this partial carbonization strategy will result in good specific capacity of Si anodes due to the improved electrical conductivity of the partial carbonization over PDA, and at the same time lead to durable cycle stability because of the ductile mechanical constraint of the retained chemical bonds from PDA in the partial carbonization condition. As a first attempt in this direction, we have chosen carbonization temperature of PDA coating at 400 °C to obtain the partial carbonization condition. The results from this first study have indeed revealed that this carbonization temperature leads to partial carbonization and can enhance the charge/discharge cycle stability of hollow core/shell Si nanoparticles. The findings are discussed in the text below.

## 2. Experimental

### 2.1. Synthesis of PDA-coated hollow core/shell Si nanoparticles

In a typical synthesis, positively-charged polystyrene (PS) nanoparticles were dispersed in DI water and ethanol solution (in 1.6:1.0 volume ratio). Next, cetyltrimethylammonium bromide (CTAB) was added as surfactant. To convert the pH value from the medium to basic condition, concentrated ammonia aqueous solution (5 wt%) was added to the solution. Then, silica source, which was tetraethyl orthosilicate (TEOS), was added and the solution was stirred at room temperature for 3 h. The solution was centrifuged and washed with DI water and ethanol for three times. The collected powder was dried in an oven at 100 °C overnight to produce SiO<sub>2</sub>-coated PS (PS@SiO<sub>2</sub>) powder. To remove the PS core, the particles were heated to 600 °C for 5 h in air under a step-wise heating program, leading to the formation of hollow silica spheres (HSiO<sub>2</sub>). Next, the HSiO<sub>2</sub> powder was mixed magnesium hydride (MgH<sub>2</sub>) powder and loaded inside a homemade Swagelok® pipe reactor inside a glovebox. The pipe reactor was heated to 700 °C for 5 h with slow heating rate to reduce HSiO<sub>2</sub> to hollow Si (HSi) spheres. The HSi powder was then washed with 1 M hydrochloric acid (HCl) for 6 h to remove residual MgO and dried at 100 °C in a vacuum oven. The HSi nanospheres were dispersed in 10 mM Tris (C<sub>4</sub>H<sub>11</sub>NO<sub>3</sub>) buffer solution (pH = 8.5, BioWorld®) for 10 min and then dopamine hydrochloride (C<sub>8</sub>H<sub>11</sub>NO<sub>2</sub>·HCl, Sigma Aldrich®) was added to the solution. The solution was stirred overnight to form the PDA coating on the surface of HSi nanospheres (HSi@PDA). The powder was collected by centrifugation, followed by multiple washing with DI water and ethanol. Then, the obtained powder was dried at 80 °C for 12 h in a vacuum oven. To partially carbonize the PDA coating, HSi@PDA powder was heated to 400 °C for

2 h under continuous flow of Ar gas with 1 °C min<sup>-1</sup> heating rate to form the final product (designated as HSi@C-400).

### 2.2. Characterization of the samples

To determine the size and morphology of nanoparticles at different stages of synthesis, samples were first coated with gold using a sputter coater and then examined using a scanning electron microscope (SEM, JEOL JSM-5900LV) in secondary electron (SE) mode with an accelerating voltage of 20 kV. JEOL JEM-3010 transmission electron microscope (TEM) was also employed to determine particle size and morphology. X-ray diffraction (XRD) was carried out using Bruker D2 Phaser in the 2θ range of 10° to 90° with Cu Kα radiation (1.54056 Å). Brunauer, Emmett and Teller (BET) specific surface area measurement was performed with a two-channel Nova Quantachrome 2200e surface area & pore size analyzer. Thermogravimetry analysis (TGA) was performed using TGA 2 (Mettler Toledo®) under air at a heating rate of 5 °C min<sup>-1</sup>. The Fourier transform infrared (FTIR) of samples were collected with Nicolet Nexus 470 FT-IR ESP spectrometer (Thermo Fisher Scientific®) in the wavenumber range of 400 to 4000 cm<sup>-1</sup>.

### 2.3. Electrochemical measurements

Electrochemical experiments were carried out in CR-2032 coin cells. The electrode's slurry was prepared by mixing HSi@C-400 nanoparticles with Super P carbon black (CB, TIMCAL®) and PAA in a weight ratio of 6:2:2 in *N*-methyl-2-pyrrolidone (NMP). The slurry was pasted on a 9-μm thick copper current collector. The painted foil was vacuum-dried in an oven at 120 °C for 12 h. The dried foil was transferred to a glovebox with both H<sub>2</sub>O and O<sub>2</sub> < 0.1 ppm and punched to 1.5 cm discs as working electrode. The loading of HSi@C-400 (the active material) per electrode was typically 1.00 mg per electrode (~0.6 mg cm<sup>-2</sup>). Pure lithium metal chips were used as both counter and reference electrodes. The electrolyte was the solution containing 1 M lithium hexafluorophosphate (LiPF<sub>6</sub>) dissolved in 1:1 volume ratio of ethylene carbonate (EC) and diethylene carbonate (DEC) with 10 vol% fluoroethylene carbonate (FEC). Celgard® 2325 microporous membrane was used as the separator. Galvanostatic charge/discharge measurements were performed with a program-controlled battery test system (Neware®, Shenzhen, China). The formation cycle entailed 5 cycles at 0.05 A g<sup>-1</sup> followed by 5 cycles at 0.1 A g<sup>-1</sup> between 0.01 and 1 V vs. Li<sup>+</sup>/Li. The voltage window for the rest of cycles was 0.1–1 V. Specific capacities and current densities were calculated based on the weight of silicon content in the active material. For comparison purpose, two additional sets of batteries were fabricated using micron-sized silicon powder (–325 mesh, 99% trace metals, Sigma-Aldrich®) and nano-sized particles (>99%, 70–130 nm, NanoAmor®) with the same fabrication condition as that of HSi@C-400 half-cells. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were executed on Parstat 4000 (Princeton Applied Research®) electrochemical workstation at a scan rate of 0.05 mV s<sup>-1</sup> and in the frequency range of 100 kHz to 1 Hz, respectively.

## 3. Results and discussions

SEM and TEM images of positively-charged PS nanospheres with round shape and average diameter of 200 nm are shown in Figs. 1a and 2a. The 3 h sol-gel reaction in the presence of CTAB surfactant and at a hydrolysis ratio of 463, which were studied before [35,45], leads to the formation of a uniform SiO<sub>2</sub> layer around PS nanoparticles (PS@SiO<sub>2</sub>) with the average shell thickness of ~25 nm (Figs. 1b and 2b). The PS core is then removed through a step-wise heating program at 600 °C to yield HSiO<sub>2</sub> nanospheres without any cracks (Figs. 1c and 2c). The significant contrast between SiO<sub>2</sub> shell and inner void space helps us determine the SiO<sub>2</sub> shell thickness as ~27 nm with slight shrinkage in the nanoparticles' diameter (~190 nm) due to eviction of chemically-bonded water and surfactant. Conversion of silica to silicon is performed with the aid of MgH<sub>2</sub> mixed uniformly with



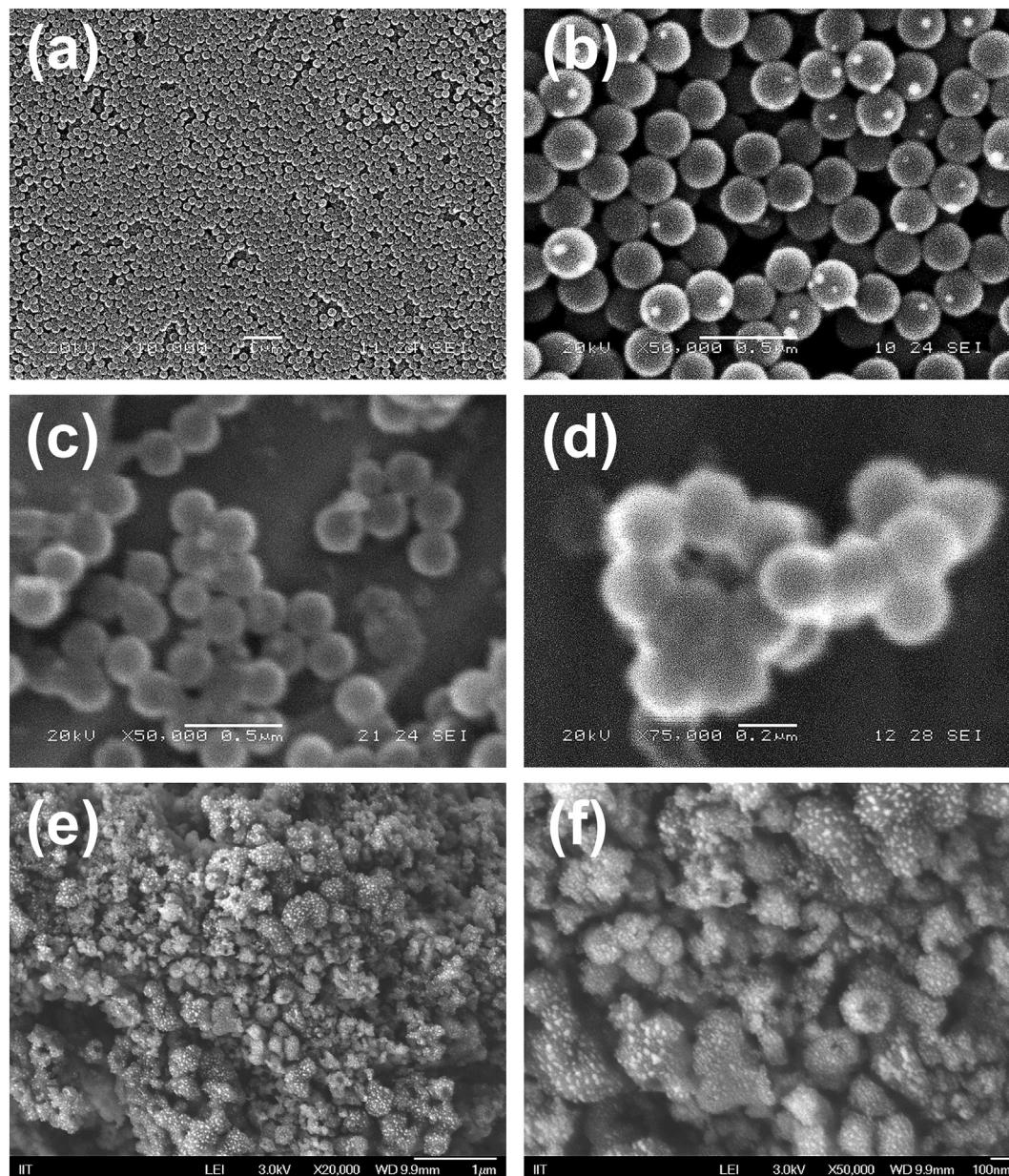


Fig. 1. SEM images of (a) positively charged PS nanoparticles, (b) PS@SiO<sub>2</sub>, (c) HSiO<sub>2</sub>, (d) HSi, and (e–f) HSi@C-400.

HSiO<sub>2</sub> and their reactions at 700 °C for 5 h with a slow heating rate. The reaction product is washed with 1 M HCl solution for 6 h to remove the byproducts of the magnesiothermic reaction such as MgO. The diameter of the obtained HSi nanospheres is about 180 nm with the Si shell thickness of ~30 nm (Figs. 1d and 2d).

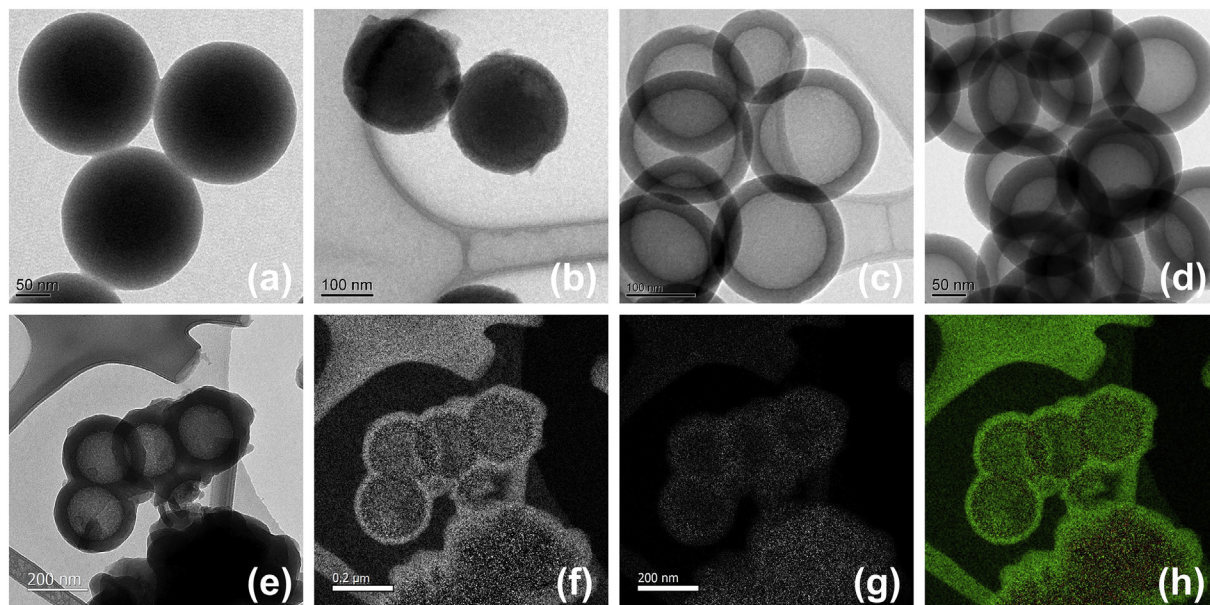
Fig. 1e and f are SEM images of carbon-encapsulated HSi nanoparticles after PODA coating and carbonization at 400 °C (HSi@C-400). Some particles are cracked during carbonization and visible in SEM images. The TEM image and elemental mapping of HSi@C-400 sample are shown in Fig. 2e to h. The HSi@C-400 nanoparticles maintain their size and shape after carbonization process without being stretched in any direction. The color mixed elemental map of silicon in red and carbon in green (Fig. 2h) clearly displays that carbon has formed a uniform 30 nm-thick layer over hollow silicon spheres. TEM images distinctly reveals that the carbon layer derived from the carbonization of PODA is more uniform than pyrrole, which we had studied before [35,45,46].

Fig. 3a presents the XRD patterns of HSi@C-400. The majority of peaks are assigned to silicon phase (PDF# 01-077-2108) and there is no evidence of the formation of any silicon-carbide compounds. The broad peak at

about 22° is assigned to amorphous carbon coating derived from low temperature carbonization of PODA. Raman spectra of HSi@C-400 is depicted in Fig. 3b, which corroborates the formation of amorphous carbon coating. Specifically, in addition to the silicon peak located at 520 cm<sup>-1</sup>, two major peaks are observed at 1350 and 1600 cm<sup>-1</sup>, which are ascribed to D and G bands, respectively [47–49]. In general, the disorder in the sp<sup>2</sup>-bonded amorphous carbon atom structures is represented by the D band, while the ordered arrangement in carbon lattice and in-plane vibrations of sp<sup>2</sup> carbon atoms are indicated by the G band [47]. Both D band and G band peaks are broad and thus heating at 400 °C does not result in the formation of high-quality few layered graphene carbon coating [48,49].

To provide additional information on the amorphous carbon coating, FTIR analysis is also conducted. To avoid any possible confusion from the incomplete conversion from hollow SiO<sub>2</sub> spheres to hollow Si spheres, if any, in the magnesiothermic reduction, FTIR analysis is performed using commercial micron-sized Si particles. In this set of experiments, micron-sized Si particles are first coated with PODA (denoted as micron-Si@PODA) at the same condition as HSi@PODA nanospheres. The PODA-coated Si particles are then carbonized at 400 °C for 2 h (termed as





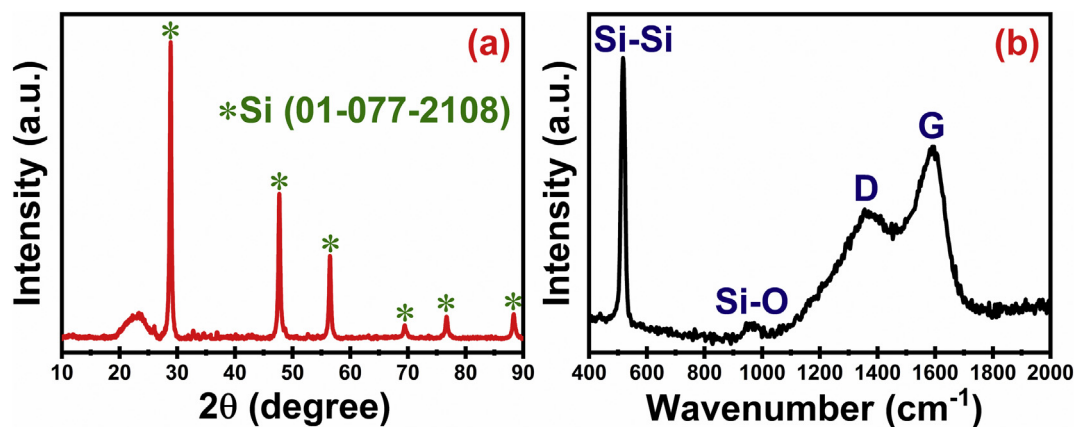
**Fig. 2.** TEM images of (a) positively charged PS nanoparticles, (b) PS@SiO<sub>2</sub>, (c) HSiO<sub>2</sub>, (d) HSi, (e) HSi@C-400, EDX mapping of (f) carbon, (g) silicon, (h) color map of elements (C: green, Si: red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

micron-Si@PODA-400 °C), again identical to the treatment experienced by HSi@C-400 particles. For comparison, some PODA-coated micron-sized Si particles are also carbonized at 800 °C for 2 h (micron-Si@PODA-800 °C). As shown in Fig. 4a, the FTIR spectrum of micron-sized Si exhibits several strong peaks related to the presence of a thin SiO<sub>2</sub> film on the surface of Si particles. The peaks at 1095 cm<sup>-1</sup> and 1180 cm<sup>-1</sup> are related to the SiO stretching vibration, while the peak at 1637 cm<sup>-1</sup> is ascribed to the OH deformation vibration [27]. After PODA coating, the peaks associated with the SiO<sub>2</sub> film at 1095 cm<sup>-1</sup>, 1180 cm<sup>-1</sup> and 1637 cm<sup>-1</sup> have all disappeared (Fig. 4b), confirming that the surface chemistry of Si particles has been changed. The new peak at 1127 cm<sup>-1</sup> is associated with the CH shearing vibration of the amide group and the CO vibration, whereas the peak at 1419 cm<sup>-1</sup> is from the phenolic C-O-H bending vibration [50–52]. The peak at 1624 cm<sup>-1</sup> is related to the stretching vibration of aromatic ring and the bending vibration of NH [50–52]. All of these new peaks in Fig. 4b confirm the presence of a PODA coating on the surface of Si particles. Interestingly, after carbonized at 400 °C for 2 h, the peaks associated with the PODA coating at 1127, 1419 and 1624 cm<sup>-1</sup> are still present (Fig. 4c). This is also the case for the sample after carbonized at 800 °C for 3 h (Fig. 4d). However, the intensities of 1127, 1419 and 1624 cm<sup>-1</sup> peaks have all decreased substantially after carbonization at 800 °C when compared with the sample with carbonization at 400 °C. These results

indicate that the major chemical bonds from PODA are still preserved with carbonization at 400 °C, whereas significant decay of the major chemical bonds from PODA has occurred with carbonization at 800 °C, confirming the partial carbonization of PODA at 400 °C.

In order to investigate the amount of carbon and silicon in HSi@C-400, TGA is carried out from room temperature to 1000 °C under the continuous flow of air (Fig. 5). HSi@C-400 sample showed significant weight loss (~30 wt%) from room temperature to ~600 °C. The weight loss from room temperature to slightly above 100 °C is mainly attributed to the removal of physically and crystallized water [53,54]. The major mass loss occurs between 300 and 600 °C, which is related to the combustion of the partially converted carbon coating. After 600 °C, HSi@C-400 starts to gain weight owing to the oxidation of hollow Si nanospheres. Based on the TGA data, we estimate the silicon content of HSi@C-400 as ~70 wt%.

Fig. 6a exhibits the nitrogen adsorption/desorption isotherm curves of HSi@C-400 nanospheres. The isotherm curve matches well with the type IV isotherm with the type III hysteresis at P/P<sub>0</sub> values ranging from 0.4 to 1.0 [55]. The BET specific surface area is found to be 135.44 m<sup>2</sup> g<sup>-1</sup>. Fig. 6b illustrates the pore diameter distribution of HSi@C-400 obtained from the Barrett, Joyner, and Halenda (BJH) method. The majority of pores are centered about 4 nm, which proves the presence of mesopore in HSi@C-400. Based on our previous measurements [45], the HSiO<sub>2</sub>



**Fig. 3.** (a) XRD pattern, and (b) Raman spectrum of HSi@C-400.

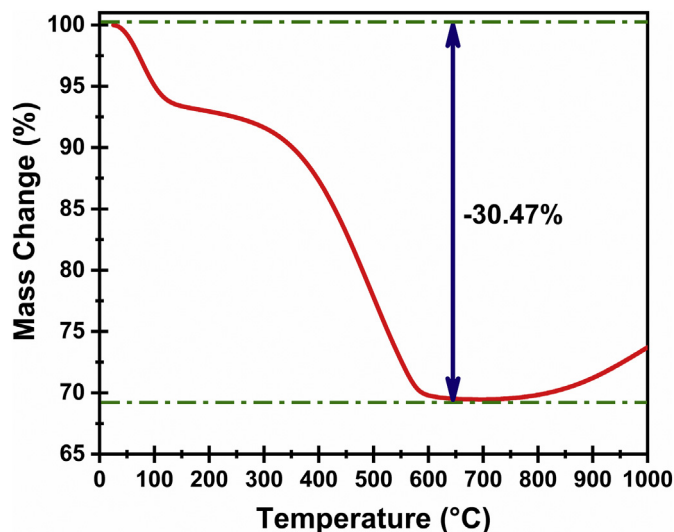


Fig. 4. TGA curve of HSi@C-400 collected under air atmosphere.

nanoparticles have a very high specific surface of  $847.283 \text{ m}^2 \text{ g}^{-1}$ , which is decreased to  $46.330 \text{ m}^2 \text{ g}^{-1}$  after the magnesiothermic reduction to form HSi nanospheres and shrinkage of the core. Thus, the increase in the specific surface area of HSi@C-400 particles over that of HSi particles suggests that the partially converted carbon coating derived from carbonization of PODA at  $400^\circ\text{C}$  is porous. The obtained porosity can favor the transport of both electrons and  $\text{Li}^+$  ions during cycling and facilitate the alloying/dealloying process [35,45,56].

The galvanostatic charge/discharge behavior of HSi@C-400 half cells is shown in Fig. 7. The formation cycles are performed at 0.05 and

then  $0.1 \text{ A g}^{-1}$  between 0.01 and 1 V vs.  $\text{Li}^+/\text{Li}$  (5 cycles for each current rate) to construct a stable SEI layer. The voltage profiles of the first 5 cycles at  $0.05 \text{ A g}^{-1}$  are plotted in Fig. 7a. As shown in Fig. 7a, the first lithiation leads to a specific capacity of  $3300 \text{ mA h g}^{-1}$ , but the first delithiation only exhibits  $2000 \text{ mA h g}^{-1}$ , resulting in a 60% coulombic efficiency (CE) in the first cycle. The low CE in the first cycle is due to the Li loss to form the SEI layer [19,35,57–59]. In the second cycle, the CE has improved to 91%, indicating continuous Li loss to form the SEI layer, but at a much slower rate than the first cycle. The delithiation specific capacity in the first 5 cycles are all above  $1800 \text{ mA h g}^{-1}$  (Fig. 7b), which is comparable with many other researches using the same lower cutoff voltage and current density [28,31,34–36,45] and consistent with the XRD and Raman data (Fig. 3) showing that  $\text{SiO}_2$  has been converted to Si after the magnesiothermic reduction.

After the current density is increased to  $0.1 \text{ A g}^{-1}$  between the 6th and 10th cycles, the delithiation specific capacity drops to below  $1750 \text{ mA h g}^{-1}$ , but still be higher than  $1600 \text{ mA h g}^{-1}$  (Fig. 7b). However, note that the specific capacity decreases continuously as the cycle number increases in the first 10 cycles (with  $\sim 20\%$  capacity loss in the first 10 cycles). This gradual loss in the specific capacity is ascribed to the loss of some HSi@C-400 particles in their participation in the redox reactions. Based on the diameters of the hollow void in the center and the Si shell in the middle of HSi@C-400 particles determined from TEM (Fig. 2), we can calculate that the volume ratio of the hollow void in the center to the middle Si shell is 47 to 100. In other words, the outer partially converted carbon shell will be subjected to tension when the middle Si shell expands by more than 47% during lithiation. Thus, if the Si shell expansion is significantly larger than 47% due to a high degree of lithiation, then the tension stress can be high enough to fracture the partially converted carbon shell. Recently, we have used an electrochemical dilatometer to measure the volume expansion of pure Si particles as a function of the degree of lithiation controlled by the lower cutoff voltage (LCV) [60], and found that the volume

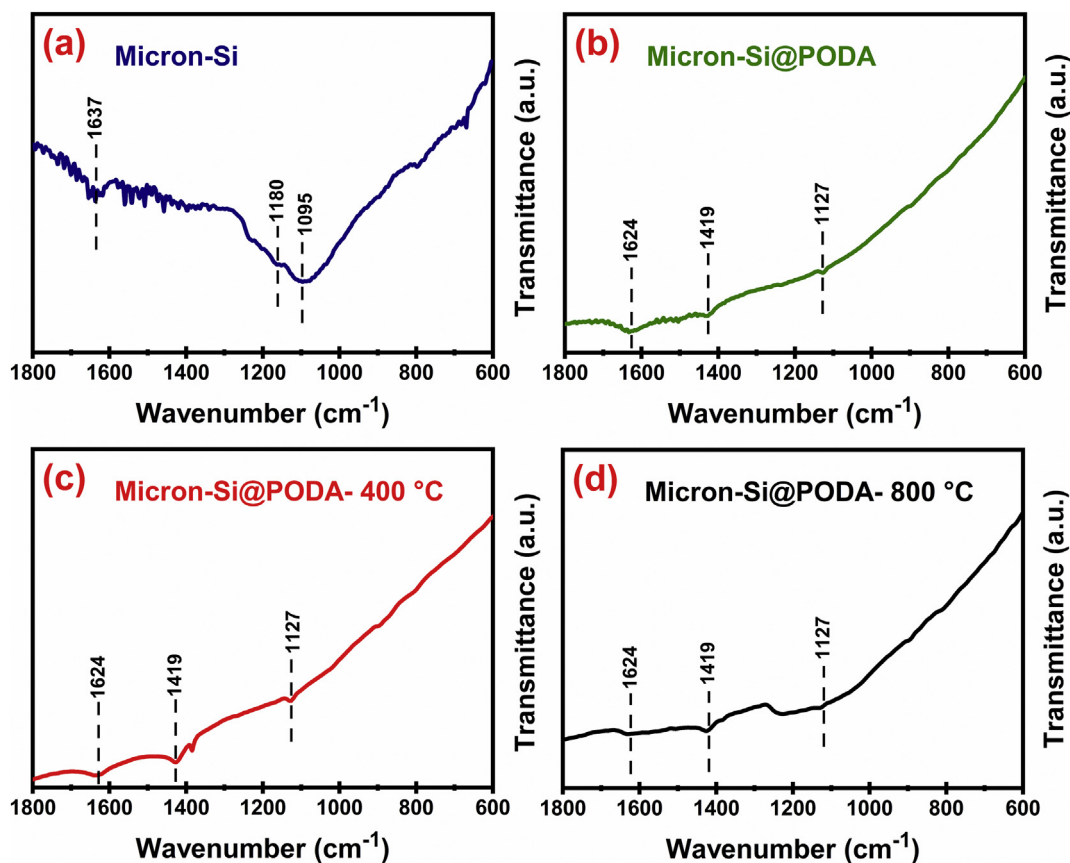


Fig. 5. FTIR spectra of micron-Si at different stages of polydopamine coating.

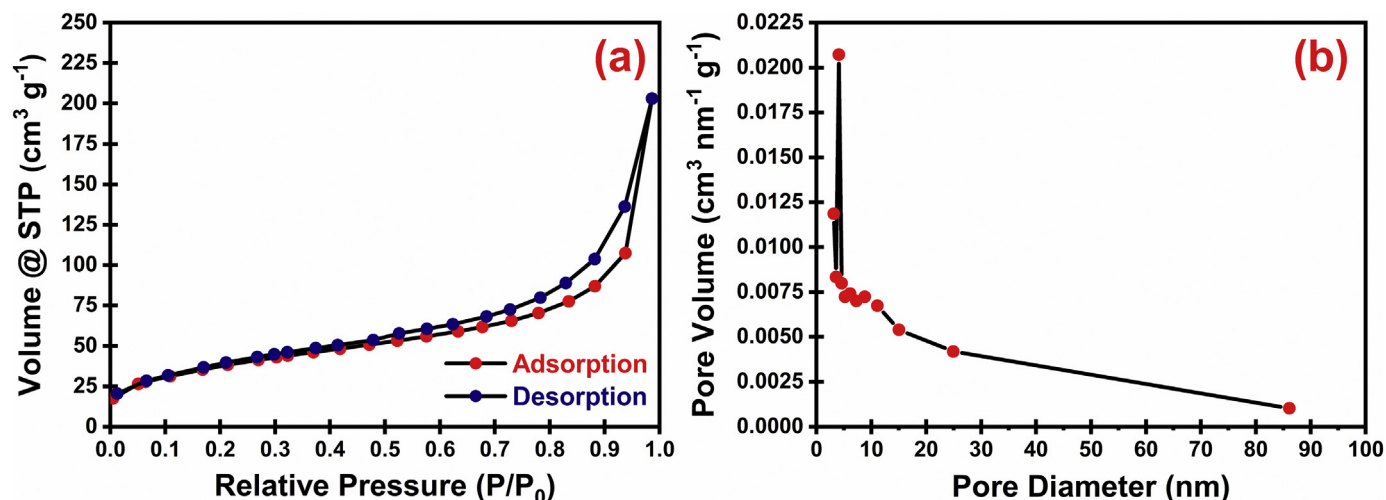


Fig. 6. (a) Nitrogen adsorption/desorption isotherms, and (b) BJH pore diameter distribution of HSi@C-400.

expansion of Si is  $\sim 88\%$  when the LCV is 0.1 V vs.  $\text{Li}^+/\text{Li}$  and becomes  $\sim 400\%$  when the LCV is decreased to 0.01 V vs.  $\text{Li}^+/\text{Li}$  [60]. Since the LCV in the formation cycles for HSi@C-400 half cells is 0.01 V vs.  $\text{Li}^+/\text{Li}$ , the volume expansion of the middle Si shell is expected to be  $\sim 400\%$  which is significantly larger than the available void space in the center (only 47% of the Si shell volume). As a result, the fracture of the outer partially converted carbon shell for some HSi@C-400 particles can take place, leading to new surface area for SEI layer formation and loss of some Si contributing to lithiation and delithiation. Both of these processes result in the low CE ( $< 97\%$ ) and gradually reduced specific capacity in the first 10 formation cycles, as shown in Fig. 7b.

After the 10 formation cycles between 0.01 and 1.0 V vs.  $\text{Li}^+/\text{Li}$ , the remaining cycles are carried out with the voltage window between 0.1 and 1.0 V vs.  $\text{Li}^+/\text{Li}$ . Because of the LCV is increased to 0.1 V vs.  $\text{Li}^+/\text{Li}$ , the volume expansion of the middle Si shell becomes much smaller ( $\sim 88\%$ ). As a result, the capacity decay slows down from the 10th to 30th cycles (with the current density at  $0.2 \text{ A g}^{-1}$ ). Further, the CE is also approaching 99.5%, much higher than those in the first 10 cycles (Fig. 7b). Moreover, the capacity decay almost disappears and the CE reaches 100% beyond the 40th cycle (with the current density at  $0.5 \text{ A g}^{-1}$ ), indicating that the design of HSi@C-400 particles with the central void space at  $\sim 47\%$  of the volume of the middle Si shell is sufficient for stable cycles with the voltage window between 0.1 and 1.0 V vs.  $\text{Li}^+/\text{Li}$ . This phenomenon is important because it reveals that HSi@C-400 particles with the central void space only 47% of

the volume of the middle Si shell is sufficient to prevent capacity decay caused by the volume expansion of the Si shell by  $\sim 88\%$ , suggesting that the partially converted carbon shell has a high tolerance in accommodating some strain without fracture during repeated lithiation and delithiation.

In sharp contrast, this is not the case for half cells made of micron-sized and nano-sized Si particles. Based on SEM images, the particle sizes of micron-sized Si powder are from 1 to  $20 \mu\text{m}$ , whereas the average size of nano-sized Si powder is about 80 nm (not shown here). As shown in Fig. 8, in the first 10 formation cycles the specific capacities of micron-sized and nano-sized Si half cells have dropped from above  $2000 \text{ mA h g}^{-1}$  to  $120 \text{ mA h g}^{-1}$  and  $375 \text{ mA h g}^{-1}$ , respectively. These specific capacities are substantially lower than  $1600 \text{ mA h g}^{-1}$  exhibited by HSi@C-400 at the 10th cycle, unambiguously revealing that the engineered void in the center of HSi@C-400 and the partially converted carbon shell have made huge improvement in minimizing the loss of specific capacity over the first 10 cycles. For the remaining cycles with the voltage window between 0.1 V and 1.0 V vs.  $\text{Li}^+/\text{Li}$ , the specific capacity of the micron-sized Si half cell is near zero, while the corresponding value of the nano-sized Si half cell is  $\sim 120 \text{ mA h g}^{-1}$  at  $0.2 \text{ A g}^{-1}$  and near zero at  $0.5 \text{ A g}^{-1}$ . All of these values are drastically lower than  $\sim 500 \text{ mA h g}^{-1}$  exhibited by HSi@C-400 under the same charge/discharge protocol (Fig. 7-b), again demonstrating that the engineered void in the center of HSi@C-400 and the partially converted carbon shell are important in retaining the specific capacity of Si material.

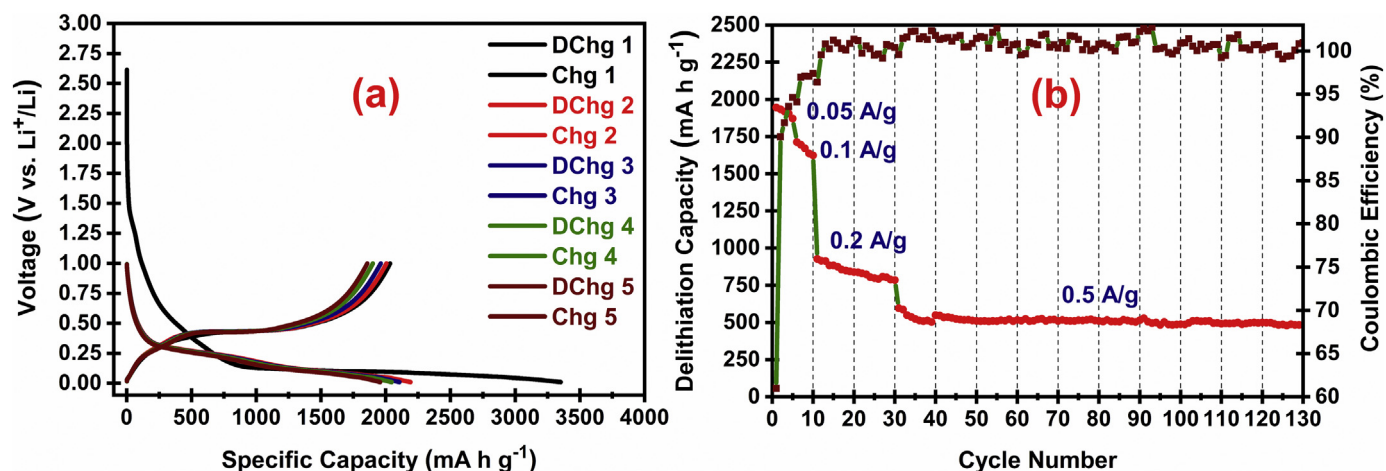


Fig. 7. (a) Voltage profile and (b) cycling performance of HSi@C-400 half cells with different voltage windows (the first 10 cycles between 0.01 and 1.0 V and the remain cycles between 0.1 and 1.0 V vs.  $\text{Li}^+/\text{Li}$ ). The current densities for cycles are indicated in (b).



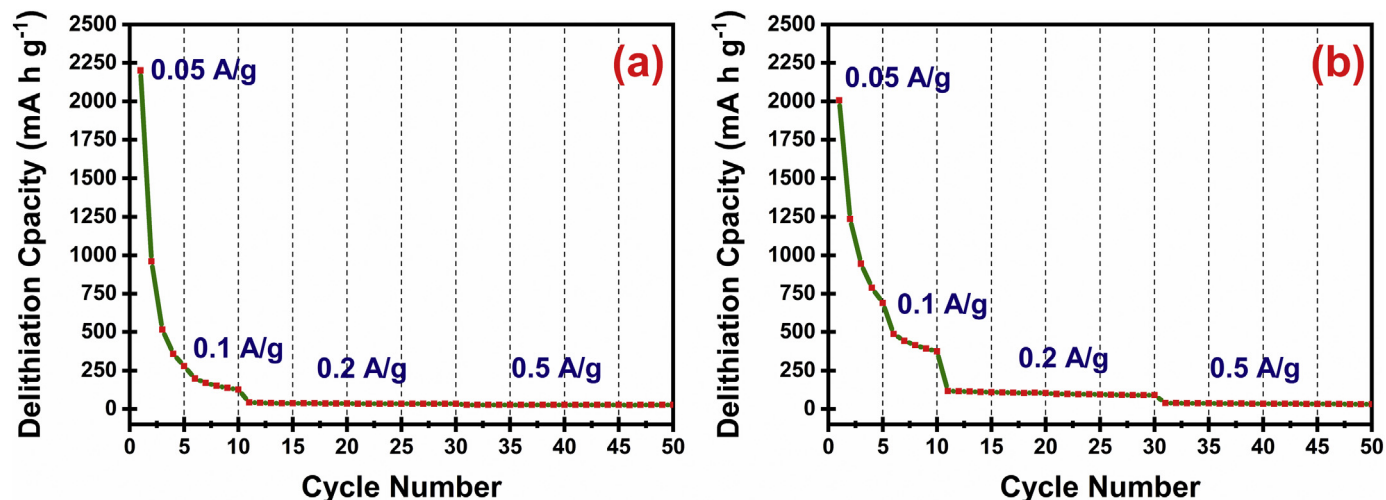


Fig. 8. Cycling performance of (a) Sigma Aldrich® micron-sized and (b) NanoAmor® nano-sized silicon particles. The charge/discharge protocol is identical to that of HSi@C-400 half cells shown in Fig. 7.

To further understand the properties of HSi@C-400, CV test has been conducted. Fig. 9a depicts the CV curves of a HSi@C-400 half cell cycled between 0.005 and 1.5 V vs.  $\text{Li}^+/\text{Li}$  at a scan rate of  $0.05 \text{ mV s}^{-1}$ . The sluggish

kinetics of lithiation/delithiation of silicon dictates a very slow scan rate to increase scan resolution and detect all possible peaks. The cathodic peak between 0.005 and 0.25 V is associated with the lithiation of silicon and

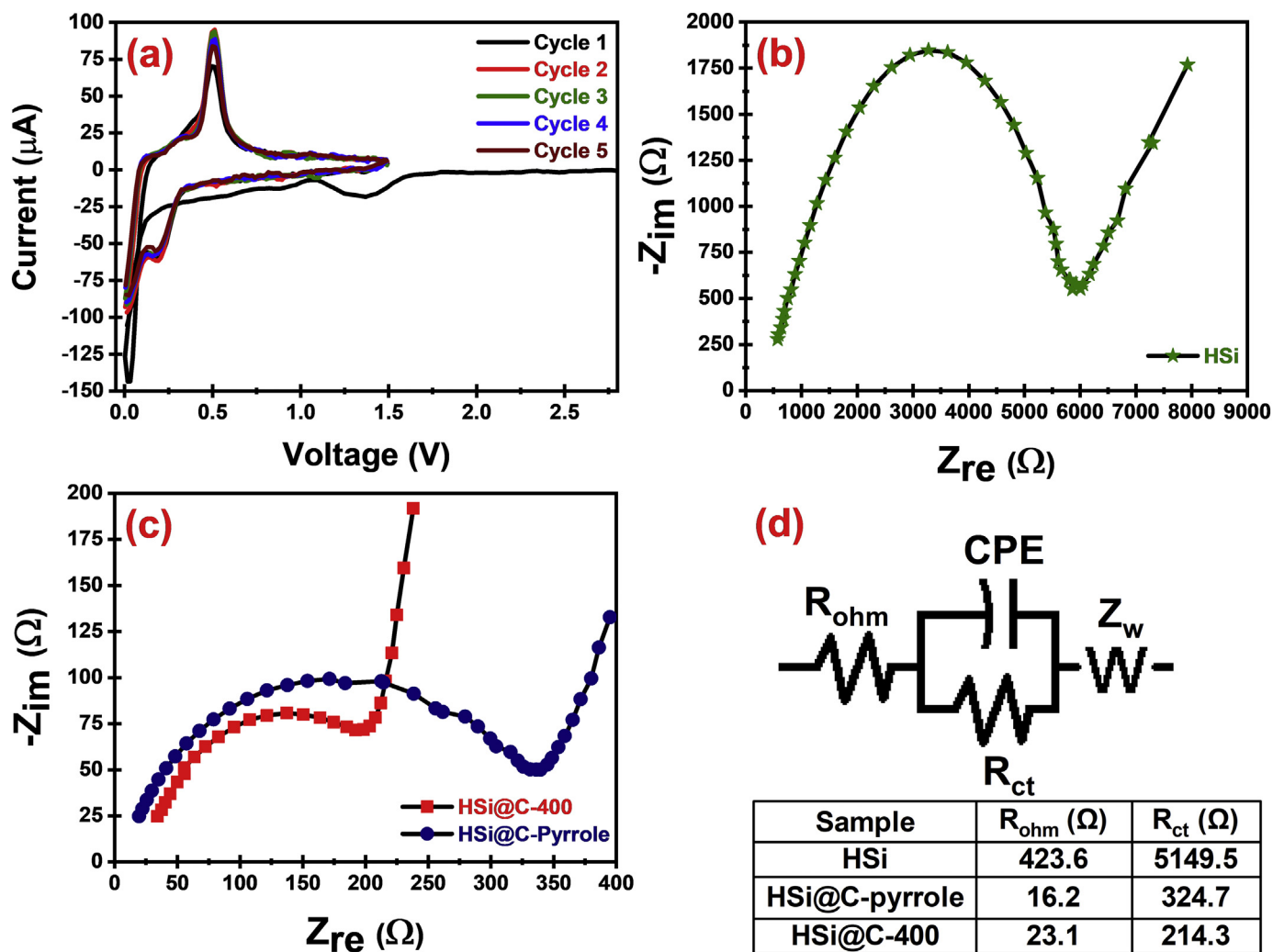


Fig. 9. (a) CV curve of a HSi@C-400 half cell, (b) Nyquist plot of a HSi nanospheres half cell, (c) Nyquist plots of a HSi@C-400 half cell and a half cell of HSi nanospheres coated with pyrrole and then carbonized at  $600^\circ\text{C}$  for 5 h (denoted as HSi@C-pyrrole), and (d) the equivalent circuit  $R(QR)W$  along with the  $R_{\text{ohm}}$  and  $R_{\text{ct}}$  values derived from the equivalent circuit analysis of the EIS data for each cell.

formation of  $\text{Li}_x\text{Si}$  alloy. In the anodic scan, the delithiation reaction is expressed by a small hump located at 0.35 V followed by a sharp peak centered at 0.50 V. These redox peaks are consistent with other Si anode studies [33,35,36,46,61], confirming the successful conversion of hollow  $\text{SiO}_2$  to hollow Si nanospheres in the magnesiothermic reduction and the lithiation/delithiation properties observed in Fig. 7 coming from the middle Si shell. It is noted that the peak current density and integrated area intensity do not vary much after the first cycle, proving the reversibility of lithiation/delithiation reactions along with the fact that the SEI layer growth rate is slow after the first cycle. In addition, no additional peaks are observed related to the reaction of  $\text{Li}^+$  ions with the partially converted carbon shell. This reveals that the partially converted carbon shell only acts as a conductor and applies mechanical constraint to the middle Si shell without participation in the redox reaction.

To find out whether the partially converted carbon shell can provide sufficient electrical conductivity or not, EIS is conducted on half cells. For comparison purpose, HSi nanospheres half cells have also been fabricated and subjected to EIS measurement. The Nyquist plots of both cells are collected after 24-h soaking before cycling and shown in Fig. 9b and 9c. In addition, the Nyquist plot of the half cell of HSi nanoparticles coated with pyrrole and carbonized at 600 °C for 5 h, measured in a previous study [35], is also included in Fig. 9c for comparison. All Nyquist plots possess one depressed semicircle followed by an inclined line at the low frequency region. It is known that the intercept of the semicircle with the real axis at the highest frequency represents the ohmic resistance of all components of the half cell, including current collectors, separator, electrolyte, and cell connectors [35,61,62]. The semicircle, which occurs at high to medium frequencies, is associated with both charge transfer and SEI layer resistance, while the inclined line at low frequencies is related to the diffusion-controlled Warburg impedance [35,61,62]. Since the EIS measurement is performed before charge/discharge cycles, there is little or no SEI layer resistance in these half cells and thus the semicircle is mainly associated with the charge transfer.

Using the R(QR)W equivalent circuit shown in Fig. 9d, the ohmic resistance,  $R_{\text{ohm}}$ , and charge transfer resistance,  $R_{\text{ct}}$ , of various half cells have been quantified and summarized in Fig. 9d. Note that the  $R_{\text{ohm}}$  and  $R_{\text{ct}}$  of the HSi half cell are very high ( $\sim 424 \Omega$  and  $5150 \Omega$ , respectively). However, these resistances are reduced dramatically by either the partially converted carbon coating from PODA or the carbon coating from pyrrole. The  $R_{\text{ohm}}$  ( $16 \Omega$ ) of HSi@C derived from pyrrole is smaller than that ( $23 \Omega$ ) of HSi@C-400, reflecting the advantage of a higher electrical conductivity from the pyrrole-derived carbon coating due to its higher carbonization temperature. However, the  $R_{\text{ct}}$  of HSi@C-400 is smaller ( $\sim 214 \Omega$ ) than that of HSi@C derived from pyrrole ( $\sim 325 \Omega$ ), suggesting that the partially converted carbon coating may have advantage in reducing the charge transfer resistance or this difference may come from the better adhesion of PODA coating to Si particles than pyrrole coating. Further studies are needed to clarify the mechanism for the low charge transfer resistance exhibited by HSi@C-400. Regardless of the underlying mechanism, the present EIS measurements have unequivocally revealed that the partially converted carbon coating from PODA has sufficient electrical conductivity to drastically reduce the ohmic resistance of the cell and provides low charge transfer resistance for Si anode redox reactions.

#### 4. Concluding remarks

In summary, this study has been performed as the first investigation on the effectiveness of the partially converted carbon coating from PODA to improve the cycle stability of Si anode material. It is found that the partially converted carbon coating still retains the major chemical bonds from PODA and can withstand some tensile strain induced by the volume expansion of Si during lithiation. Specifically, when the volume expansion of Si is very large ( $\sim 400\%$ ), the specific capacity of HSi@C-400 half cells drops very fast because of the fracture of HSi@C-400 particles. However, when the volume expansion of Si is reduced to  $\sim 88\%$  by adjusting the LCV to 0.1 V vs.  $\text{Li}^+/\text{Li}$ , the capacity decay of HSi@C-400 over cycles almost disappears

and the coulombic efficiency reaches 100%. This cycle stability can be attributed to the tolerance of the partially converted carbon coating in accommodating some tensile strain without fracture even though the central void space in HSi@C-400 is only 47% of the Si shell volume (smaller than the volume expansion of  $\sim 88\%$  experienced by the middle Si shell). CV studies reveal that the partially converted carbon shell only acts as a conductor without participation in the redox reaction. EIS measurements show that the partially converted carbon coating can provide sufficient electrical conductivity for lithiation and delithiation of HSi@C-400 half cells and drastically reduce the charge transfer resistance for the redox reactions of HSi@C-400. This first study of the partially converted carbon coating from PODA offers a new direction for systematic studies in the future as a means to provide a coating on Si material with sufficient electrical conductivity along with capability to withstand some tensile strain during the volume expansion of Si, thereby improving the cycle stability of Si anodes.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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