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Three – Dimensionally Ordered Macroporous Amorphous C/TiO₂ Composite Electrodes for Lithium-ion Batteries

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A facile method utilizing colloidal templating and sucrose as a carbon precursor is used to synthesize highly ordered, porous inverse opal structures as C/TiO₂ nanocomposites. Material characterization shows amorphous TiO₂ and a large pore size of ~400 nm allowing for enhanced electrolyte penetration. C/TiO₂ inverse opals materials as electrodes in Li-ion battery half cells demonstrate discharge and charge capacities of ~870 mAh g⁻¹ and 470 mAh g⁻¹, respectively, at a current density of 150 mA g⁻¹. The enhanced capacities, which surpass theoretical limits for TiO₂ and carbon based on intercalation reactions, are analyzed under voltammetric conditions to assess relative contributions to capacity from diffusion-limited intercalation and capacitive charge compensation reactions. The porous structure contributes to excellent capacity retention, rate performance and improved Coulombic efficiency (99.6% after 250 cycles), compared to individual carbon and TiO₂ inverse opals.

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The development of high-performance lithium-ion batteries (LIBs) has revolutionized modern portable electronics and electric vehicle technology.¹⁻⁴ The key to the outstanding performance of LIBs lies in the design and engineering of their electrodes.⁵⁻⁸ As the demand for higher energy density, faster charging capabilities and longer cycle life continues to grow, the need for advanced electrode materials^{9,10} and designs becomes increasingly crucial. Large-scale production of carbon-based materials has made them a prevalent choice as anodes in LIBs, widely used in both portable and stationary devices due to their cost-effectiveness, abundance, electrical conductivity, and low toxicity.¹¹⁻¹³ However, carbon based materials suffer great danger from dendrite formation due to their low intercalation potential, which can cause poor cycling stability, and safety issues. Conversely, TiO₂ has shown good chemical and physical properties and has garnered attention as a promising material in LIBs¹⁴⁻¹⁶ and other electrochemical technologies, nonetheless, TiO₂ suffers from limited Li-ion and electron transport capabilities which results in low capacity retention and poor rate performances.^{17,18}

Composites materials have garnered significant attention as a means to harness the advantages of multiple materials, often resulting in synergistic outcomes.¹⁹⁻²³ Nevertheless, many commercial materials are slurry-based, comprising of active material particles, binders and conductive additives that are randomly arranged and densely packed, affording limited control over their structural attributes.²⁴ They exhibit an adverse relationship between tortuosity and porosity, leading to a trade-off between energy density and power density.^{25,26} Consequently, nanostructuring both TiO₂ and carbon materials have been investigated as a method of improving Li⁺ diffusion and electrical conductivity as well as increasing specific capacity, and examining the relative influence of these parameters.²⁷⁻³³ Three-dimensional ordered macroporous (3DOM) materials represent a promising avenue in this pursuit, characterized by interconnected pore and wall structures with wall thicknesses of a few tens of nanometers.³⁴⁻³⁹ Among these materials, inverse opals (IOs) are a subtype of 3DOMs, formed via

a sacrificial template of polymer spheres such as polystyrene.^{40,41} IOs offer the benefit of shorter diffusion lengths for lithium ions and can improve charge transfer rates because of a larger surface area. The porous architecture facilitates rapid Li⁺ movement and diffusion within the electrolyte, all while preserving the structural integrity, thus preventing volume swelling or material degradation. Notably, IOs can be prepared directly onto the current collector and so removes the need for any binders or additives.

In this report, C/TiO₂ composite inverse opal electrodes with a robust 3D structure and high surface area were synthesized using a solvent infiltration method. Structural characterization in the form of X-ray diffraction (XRD) and selected area electron diffraction (SAED) reveals the amorphous nature of the material. We investigate the effect of combining carbon and TiO₂ by conducting a comparative electrochemical analysis of the composite IO electrode alongside their individual IO counterparts. The electrochemical performances of both materials are analyzed by cyclic voltammetry (CV), galvanostatic cycling (GCPL) and rate testing. Our findings demonstrate that the C/TiO₂ IOs offer increased capacities and improved capacity retention over 250 cycles compared to pure TiO₂ and carbon IOs. Our composite electrodes exhibit stable Coulombic efficiency even at high current densities, showcasing very good high-rate performance. Furthermore, post-mortem evaluation underscores the structural stability of the IOs, as they maintain their structural integrity after cycling.

Experimental

Materials preparation.—The substrates used were stainless steel (SS) discs (grade 304) with a diameter of 15.5 mm. The opal template was fabricated using the evaporation induced self-assembly (EISA) method, which involved suspending the SS discs in a 0.2% solution of polystyrene spheres (500 nm diameter) and deionized water and placing in a convection oven at 60 °C overnight. TiO₂ and carbon IO samples were prepared for the purpose of conducting structural and crystallinity comparison analyses, as well as for making electrochemical comparisons with the composite materials.

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C/TiO₂ IO preparation.—A 0.1 M solution of titanium(IV) chloride tetrahydrofuran (TiCl₄.2THF) was prepared in IPA while the carbon precursor solution consisted of sucrose, ethanol (EtOH), deionized water and sulphuric acid (18 M, Sigma Aldrich). These were mixed in mass ratios of 1:35.5:5:0.18, respectively. The dried PS sphere templates were then infilled by drop casting a volume of the carbon precursor ($\sim 15 \mu\text{l}$) followed by an equal volume of the TiO₂ precursor. The samples were placed in a convection oven at 70 °C for 25 min before being heated to 100 °C for 5 h in air. After 5 h the samples were placed in a tube furnace under Ar and heated to 500 °C at a ramp rate of 5 °C min⁻¹. The samples were held at 500 °C for 2 h.

Carbon IO preparation.—The dried PS spheres were infilled with $\sim 30 \mu\text{l}$ of the sucrose solution before being placed in a convection oven at 70 °C for 25 min. The carbon samples were then heated to 100 °C for 5 h in air before being heated to 900 °C under Ar and held for 2 h.

TiO₂ IO preparation.—The dried PS spheres were infilled with $\sim 30 \mu\text{l}$ of the TiCl₄.2THF solution before being placed in a convection oven at 70 °C for 25 min. The samples were then heated to 500 °C in air at a ramp rate of 5 °C min⁻¹ and held for 1 h.

Material characterization.—SEM analysis was performed on FEI Quanta 650 FEG high resolution SEM at an accelerating voltage of 10 kV. EDS analysis was performed using a FEI Quanta 650 FEG high resolution SEM at an accelerating voltage of 20 kV. EDS mapping was performed on Zeiss Supra 40 high resolution SEM at an accelerating voltage of 20 kV. SEM images and feature dimensions were analyzed using ImageJ software. Raman scattering was performed on an Ocean Optics QE65PRO Raman Spectrometer using a 40 mW Ar⁺ laser at 532 nm excitation. The laser was focused onto the samples using a 40 $\times$ objective lens and spectra were collected using a CCD camera. X-ray diffraction (XRD) was conducted using a PANalytical XPERT PRO PW3050 diffractometer using a Cu anode, K α radiation with wavelength λ =

0.15406 nm, operation voltage 40 kV, current 20 mA, with the samples being scanned from $2\theta = 5^\circ$ –80°. TEM analysis was conducted using a JEOL JEM-2100F TEM operating at 200 kV.

Electrochemical characterization.—All electrochemical characterization was performed using BioLogic VSP Potentiostat/Galvanostat. All IOs were investigated in a half cell configuration against a pure Li counter, using a stainless-steel PAT-cell from EL-Cell in a two-electrode configuration. The electrolyte used was lithium hexafluorophosphate solution, in ethylene carbonate and diethyl carbonate, 1.0 M LiPF₆ in EC/DEC=50/50 (v/v), battery grade from Sigma Aldrich. The separator used was glass microfiber from Whatman Grade GF/A cut to size. The typical loading mass of the samples were between 0.4 mg–0.7 mg. C/TiO₂ electrochemical tests were investigated in a potential window of 3.0 V–0.01 V. Supplementary electrochemical tests for carbon and TiO₂ IOs were investigated in a potential window of 3.0 V–0.01 V unless stated otherwise. Cyclic voltammetry was performed at various scan rates for C/TiO₂ and galvanostatic cycling was performed using various specific currents as mentioned in this report (0.05 mV s⁻¹–1000 mV s⁻¹, 75 mA g⁻¹–450 mA g⁻¹).

Results and Discussion

Material characterization.—The carbon/TiO₂ inverse opal (IO) samples were prepared by evaporation induced self-assembly (EISA) as described by Colvin et al. with a volume fraction of 0.2%.⁴² The polystyrene sphere opal templates were then infilled with 15 μl of the sucrose solution and 15 μl of the TiO₂ precursor. The samples were then dried at 70 °C for 30 min to evaporate the solvents in the precursor followed by a pre-carbonization step which involved heating the samples to 100 °C in air and held for 5 h. The samples were then placed in a tube furnace and heated to 500 °C under Ar and held for 2 h. The sacrificial sphere template decomposed with the high temperature which allowed the IO structure to form and produce highly ordered porous structures which can be seen in the SEM images in Figs. 1a–1d. The thickness of the inverse

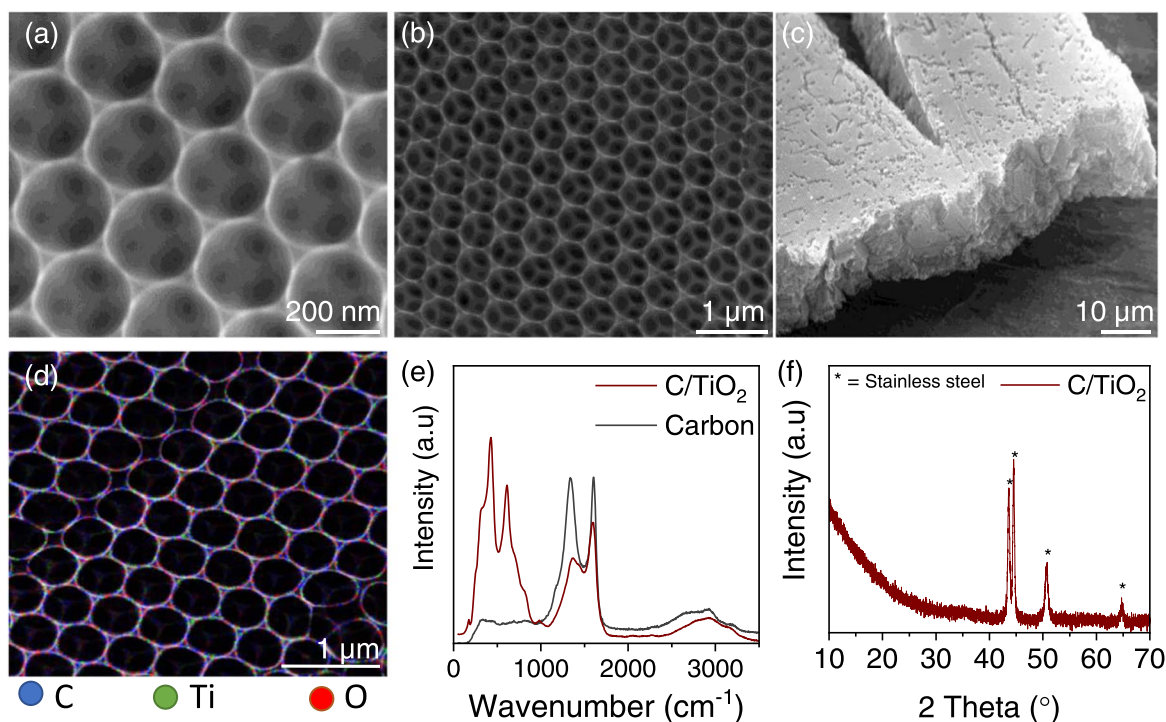


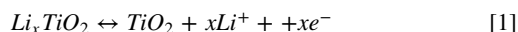
Figure 1. (a)–(c) SEM images of C/TiO₂ inverse opals at various magnifications. (d) EDX mapping of key elements overlaid onto an SEM image. (e) Raman spectra of C/TiO₂ IO and carbon only IO, showing rutile TiO₂ and D and G bands for carbon. (f) XRD pattern depicting amorphous C/TiO₂, peaks labelled * correspond to the stainless-steel substrate.

opal structure is $\sim 17 \mu\text{m}$ thick and contains pores with an average diameter of 363 nm (shown in Supplementary material, Fig. S1). The various layers that form the (111)-oriented inverse of the apparent face centered cubic (fcc) opal template can be seen through the pores of the samples from the SEM images. The atomic ratio of carbon to TiO_2 was found to be between 8:1 and 10:1, the variance in ratio may be due to remnant or adventitious carbon from the polystyrene spheres.

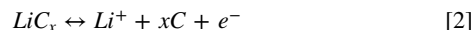
Raman scattering spectroscopy in Fig. 1e detected peaks at 173.8 cm^{-1} , 427.9 cm^{-1} , 611.3 cm^{-1} , 801.3 cm^{-1} and 316.7 cm^{-1} for modes B_{1g} , E_g , A_{1g} , B_{2g} and second order scattering indicative of rutile TiO_2 . Peaks at 1372.7 cm^{-1} and 1597.2 cm^{-1} show the D (disorder) and G (graphitic) bands for carbon, respectively. The G band is due to the in-plane stretching of C sp^2 bonded atoms for both chain and rings, while the D band indicates disorder is present, and its intensity is correlated to the presence of sixfold aromatic rings.⁴³ The I_D/I_G ratio was found to be 0.71 compared to the I_D/I_G ratio of 1.00 for the carbon-only IO spectra. This decrease in ratio indicates a reduction in order and may indicate increasing amorphization of the carbon. X-ray diffraction (XRD) measurements of the IO structure suggested that the materials are predominantly amorphous, showing no distinct peaks in the XRD pattern other than those for the stainless-steel substrate. Localized laser-induced heating allowed us to see the crystallized form of both materials, but the as-prepared composite IO is an amorphous material.^{44,45} Notably the XRD patterns align with the electron diffraction patterns depicted in Fig. 2.

Transmission electron microscopy (TEM) analysis was employed to gain further insight into the porous structure of the C/ TiO_2 composites. In Figs. 2a, 2b, TEM images of the C/ TiO_2 composite at different magnifications reveal a hierarchical porous structure characterized by macroscopic pores. The wall diameters were measured to be $\sim 30 \text{ nm}$ on average, compared to $\sim 26 \text{ nm}$ for carbon IOs and $\sim 12 \text{ nm}$ for TiO_2 IOs (shown in Supplementary material, Fig. S2). The high-resolution TEM (HRTEM) image in Fig. 2c has no discernible lattice fringes indicating the amorphous nature, which is confirmed by the selected area electron diffraction (SAED) pattern in Fig. 2d. By comparison, pure TiO_2 -only IOs are crystalline in the anatase phase, and pure carbon-only IOs are amorphous. Further HRTEM details on the crystalline TiO_2 -only IOs are shown in Supplementary material, Fig. S3. The dark-field TEM image and the corresponding EDS elemental mapping images can be seen in Figs. 2e–2h, revealing a notably uniform dispersion of carbon (C), oxygen (O), and titanium (Ti) species. Figure 2i show an SEM images of the C/ TiO_2 IO material and the resulting EDS line scan, revealing a generally homogenous and consistent dispersion of carbon (C), oxygen (O), and titanium (Ti) species across the trace line.

Electrochemical characterization.—The electrochemical behavior of the material was characterized in a half cell system against a Li metal counter electrode. Figure 3a shows the cyclic voltammetry (CV) curves at a scan rate of 0.05 mV s^{-1} in the potential window 3 V—0.015 V. Four regions of interest in the cathodic scan include the peaks at 1.4 V, 1.28 V, 0.73 V and the sloping region from 0.49 V—0.015 V. These peaks correlate to major lithiation reactions with C/ TiO_2 . The cathodic reduction peak at 1.4 V and the anodic oxidation peak at 1.86 V are associated with the lithiation/delithiation of TiO_2 , which follows the Eq. 1:



Evidence of SEI layer formation is found at 1.3 V as this peak is only visible for the first cycle. The peak centered at 0.73 V suggests lithium insertion into the carbon material and is observed in CVs for carbon only IOs (Fig. 3b). The sloping region from 0.49 V to 0.015 V correlates to the lithiation of carbon, which follows the reaction Eq. 2:



The anodic peak at 1.16 V is attributed to the delithiation of carbon, and the delithiation of TiO_2 is shown by the peak at 1.86 V. While TiO_2 is described as an intercalation mode material, hard carbons react with lithium by capacitive ionization/deionization and adsorption/desorption processes. C/ TiO_2 IOs were compared to carbon IOs that were cycled between 2 V—0.01 V in Fig. 3b, highlighting the increased current density arising from the addition of TiO_2 . To investigate charge storage properties for C/ TiO_2 , CVs were taken at various scan rates from 0.1 mV s^{-1} to 1000 mV s^{-1} in the voltage range of 0.015 V to 3 V as shown in Fig. 3c. The total stored charge can be separated into faradaic and non-faradaic processes, faradaic processes involve a transfer of charge at the electrode-electrolyte interface, such as intercalation and/or alloying, while non-faradaic processes^{46–50} involve electrostatic interactions without significant chemical changes.⁵¹

Capacitive effects can be characterized by analyzing the CV at various scan rates according to⁵²

$$i(V, t) = av^b \quad [3]$$

where i is the current (mA), v is the scan rate (mV/s) and a , b are adjustable values. The b -values can be obtained by setting a log on both sides of Eq. 3,

$$\log i = \log a + b \log v \quad [4]$$

and finding the slope (Figs. 3e, 3f). When $b = 0.5$, the process is considered diffusion limited and when the b -value approaches 1.0, capacitive behavior is dominant.⁵³ In Fig. 3e we show the plot of $\log(i)$ vs $\log(v)$ for the 3 cathodic peaks observed in the CV, and for a range of currents from the CVs in Fig. 3f. All 3 voltage points show a b -value below 0.5, indicating that the current response is primarily due to intercalation reactions rather than capacitive.

The total current (i) at a specific potential (V) is the sum of both the diffusion-controlled and capacitive reactions according to:

$$i(V, t) = k_1v + k_2v^{1/2} \quad [5]$$

where k_1v and $k_2v^{1/2}$ correspond to the current attributed to capacitive and diffusion-controlled process respectively. By rearranging this equation to

$$\frac{i}{v^{1/2}} = k_1v^{1/2} + k_2 \quad [6]$$

we can find k_1 and k_2 through the linear fit of $\frac{i}{v^{1/2}}$ vs $v^{1/2}$. It is then possible to distinguish between currents arising from Li^+ insertion and those occurring from capacitive-like processes.^{54,55} Figure 4 shows the voltage profiles for the intercalation (red) and capacitive (green) currents compared to the measured current (grey) for scan rates 0.1 mV s^{-1} – 1000 mV s^{-1} . Diffusion processes account for $\sim 99.5\%$ of the current measured for the 0.1 mV s^{-1} scan as per Figs. 4a, 4f, this decreases slightly to $\sim 98\%$ for the 1 mV s^{-1} scan showing little contribution from capacitive processes. This is in excellent agreement with the b -values calculated for the cathodic peaks which were on or below 0.50. Once a scan rate of 100 mV s^{-1} is reached (Figs. 4d, 4f) we observe pseudocapacitive behavior at the surface, with $\sim 21\%$ of the current arising from capacitive-like processes. Intercalation is a slower process than capacitive charge compensation at the surface,⁵³ which could explain the drop in specific capacity under fast voltage scanning conditions to 9.8 mAh g^{-1} as shown in Supplementary material, Fig. S4. Specific capacity for the cell was found using the following equation,

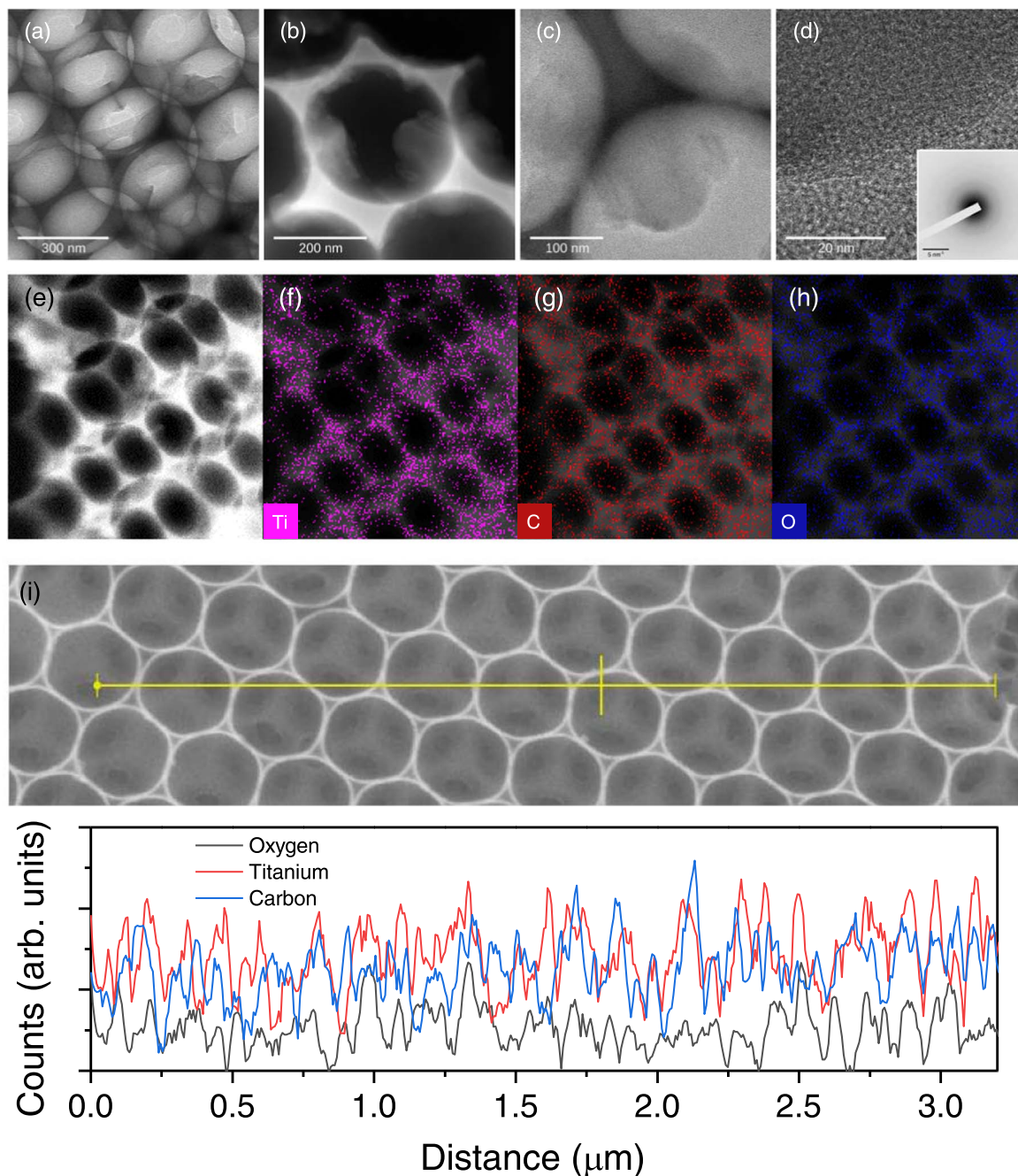


Figure 2. (a), (b) Bright and dark-field TEM images of C/TiO₂ IO material showing the interconnected structure and a local pore. (c) HRTEM image of C/TiO₂ material showing no distinct lattice fringes and (d) resulting SAED indicating dominant amorphous nature. (e) Dark field TEM of C/TiO₂ IO and resulting EDS mapping showing distribution of (f) titanium, (g) carbon, and (h) oxygen. (i) SEM image and corresponding EDS line scan (yellow line shows the line scan trace) showing atomic ratios of carbon (blue), oxygen (grey) and titanium (red).

$$C = \frac{1}{mv(V_c - V_a)} \int_{V_a}^{V_c} I(V) dV \quad [7]$$

where V_c and V_a are the cathodic and anodic voltage limits respectively, m is the mass loading of the electrode and v is the scan rate. At 1000 mV s^{-1} we find almost 50:50 contribution from capacitive and diffusion reactions. The presence of capacitance contributions occurring with an opposite polarity of current (or beyond the region covered by the measured current in grey), results from the deconvolution process applied to the measured current. The sum total of the inferred intercalation and capacitive contributions at each given potential corresponds to the observed current (grey).

Figure 5a shows the discharge/charge voltage profile of the C/TiO₂ composites at a current density of 150 mA g^{-1} in a potential window of 0.014–3 V. All capacities were calculated based on the mass loading of the C/TiO₂ active material. Galvanostatic cycling shows initial capacities of 869 mAh g^{-1} and 472 mAh g^{-1} for the discharge and charge, respectively, with an initial coulombic efficiency (ICE) of 54.3%. This discharge capacity exceeds the theoretical capacity of both TiO₂ (336 mAh g^{-1} for LiTiO₂) and for carbon (372 mAh g^{-1} for LiC₆). The higher capacities observed mainly stem from the presence of defects formed during calcination which serve as additional charge compensation sites for lithium. A weak plateau was observed during the initial charge, from 1.50–1.15 V, followed a sloping region from 1.00 V–0.45 V, and another

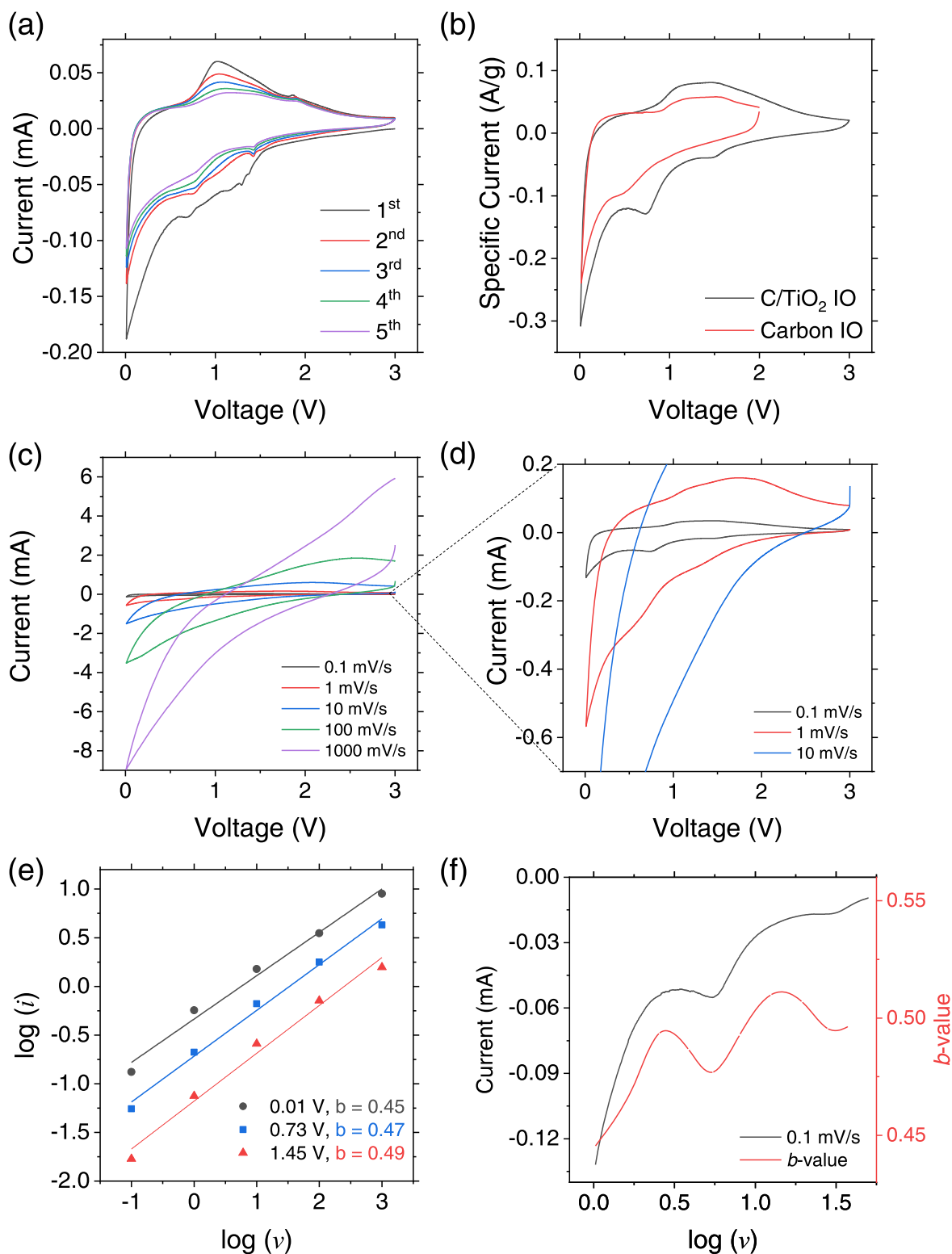


Figure 3. (a) CV of C/TiO₂ IO for the first five scan at scan rate 0.05 mV s⁻¹. (b) CV of C/TiO₂ IO compared to carbon only at 0.1 mV s⁻¹. (c) CV of C/TiO₂ IO at various scan rates from 0.1–1000 mV s⁻¹, (d) is magnified (c) to show curves at 0.1 and 1 mV s⁻¹. (e) *b*-values for log(*i*) as a function of log(*v*) for C/TiO₂ IOs at key insertion voltages (f) calculated *b*-values for C/TiO₂ IO overlaid on the first cathodic scan at a scan rate of 0.1 mV s⁻¹.

sloping region extending to the lower potential limit, which is in close agreement with the cathodic peaks observed in the CV. The low coulombic efficiency is limited to the first cycle and caused by irreversible side reactions such as the SEI layer formation. In comparison, for carbon only and TiO₂ inverse opal electrodes tested under the same conditions, the initial discharge (charge) capacities

for carbon IOs were 835 mAh g⁻¹ (299 mAh g⁻¹), with an ICE of 36% and TiO₂ IOs showed 648 mAh g⁻¹ (312 mAh g⁻¹), with an ICE of 48%. The C/TiO₂ IOs show good capacity retention with a discharge capacity of 420 mAh g⁻¹ after 100 cycles, reaching 471 mAh g⁻¹ on the 250th cycle. This slight increase in capacity may be attributed to the retention of electrolyte decomposition byproducts

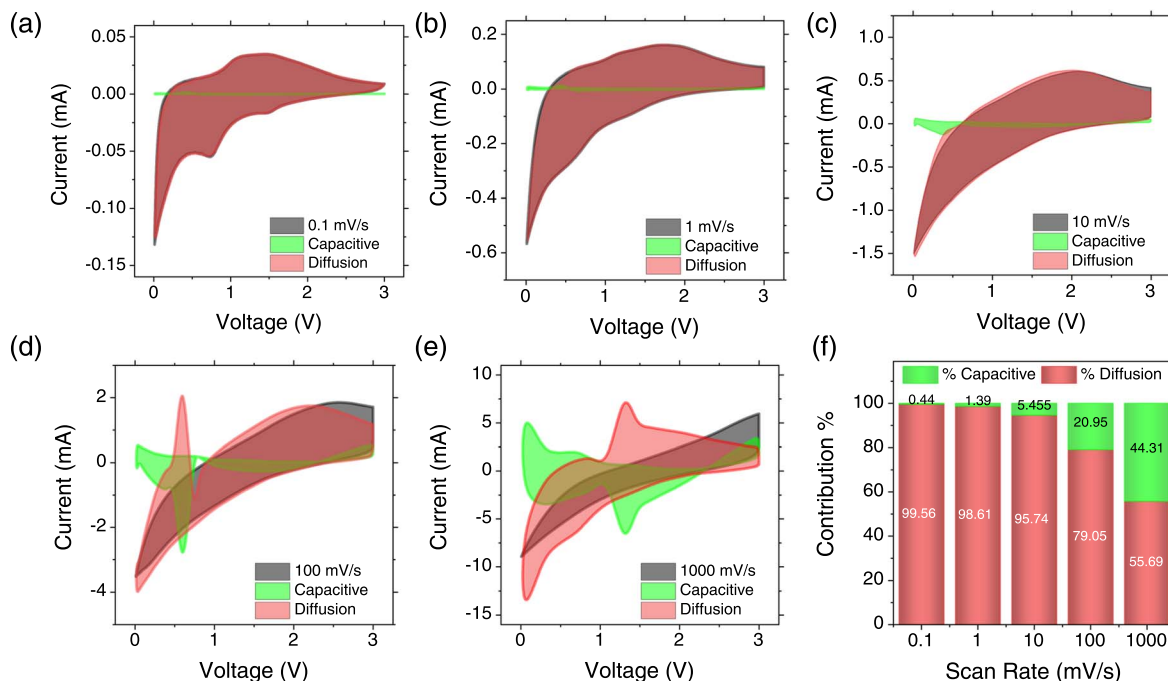


Figure 4. Intercalation (red) and capacitive (green) contributions to the total measured current (grey) for C/TiO₂ IOs at scans rates of (a) 0.1 mV s⁻¹, (b) 1 mV s⁻¹, (c) 10 mV s⁻¹, (d) 100 mV s⁻¹ and (e) 1000 mV s⁻¹. The sum of these contributions at each potential equals the actual measured current.

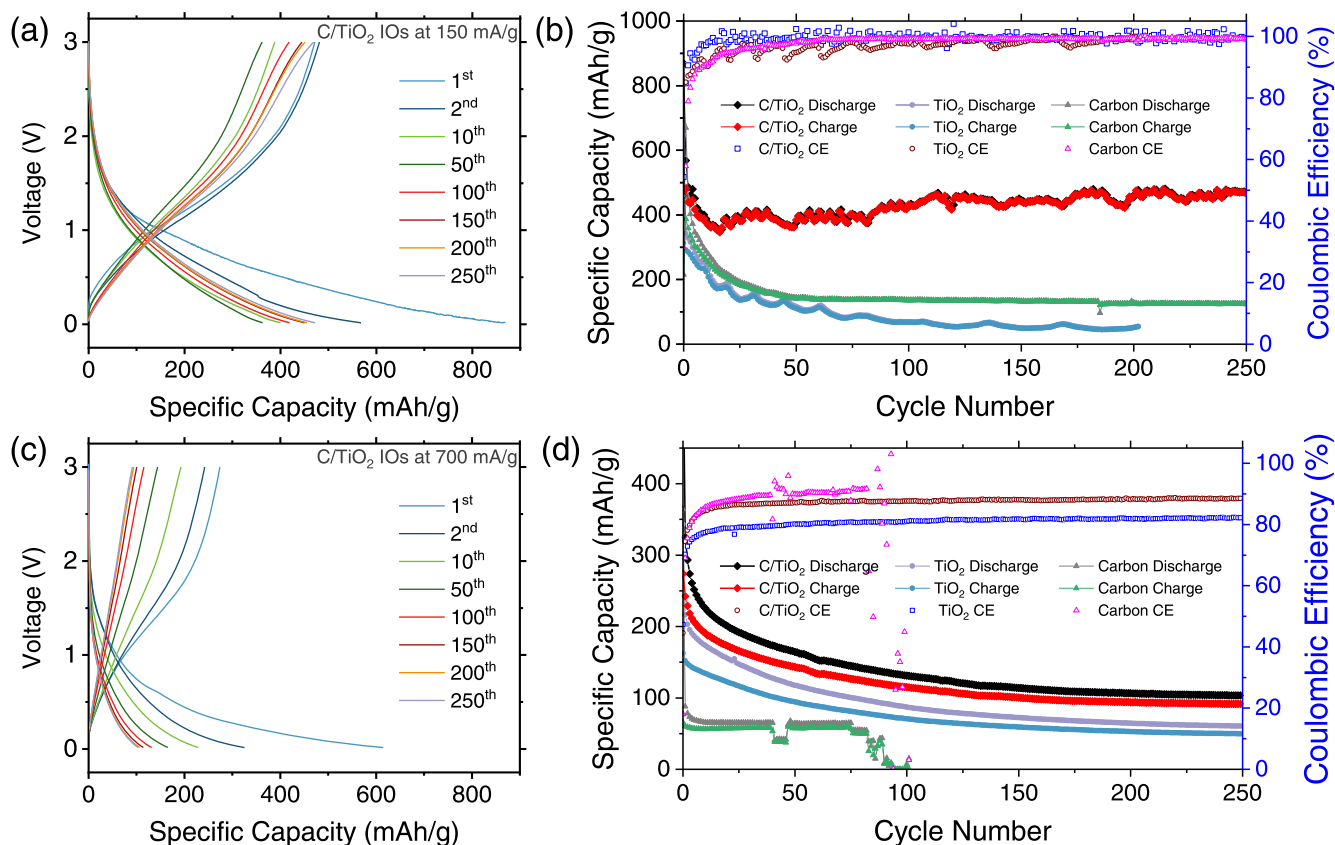


Figure 5. (a) Discharge/charge profiles for 1st, 2nd, 10th, 50th, 100th, 150th, 200th and 250th cycles at a current density of 150 mA g⁻¹. (b) Coulombic efficiency response comparing the performance of C/TiO₂, TiO₂ and carbon IOs cycled at 150 mA g⁻¹. (c) Discharge/charge profiles for 1st, 2nd, 10th, 50th, 100th, 150th, 200th and 250th cycles at a current density of 700 mA g⁻¹. (d) Coulombic efficiency response comparing C/TiO₂, TiO₂ and carbon IOs cycled at 700 mA g⁻¹.

within the walls of the macroporous structure.⁵⁶ While initial coulombic efficiency was 54.3%, this increased to 97% by the

10th cycle and had an average of 99.6% for the 250 cycles. This is an improvement on the average 98.5% coulombic efficiency recorded

for the carbon only IOs and the 96.4% CE recorded for the TiO_2 IOs. The capacity values achieved surpass previous research reported for nanocomposite carbon and TiO_2 materials prepared under comparable temperature conditions (see Supplementary material, table S1).^{57,58} This improved reversibility may be due to the porous nature of our inverse opal structures which alleviates volumetric stress arising from the swelling and contracting of the material during cycling under galvanostatic conditions where the reactions are diffusion-limited intercalation.

The galvanostatic discharge and charge curves for the composite C/TiO_2 IOs at a high current density of 700 mA g^{-1} in a voltage window of 0.014 V – 3 V are shown in Fig. 5c. Initial discharge capacity was 615 mAh g^{-1} with a charge capacity of 274 mAh g^{-1} resulting in an ICE of 44.6%. The capacity decreases to $\sim 230 \text{ mAh g}^{-1}$ by the 10th cycle, and experiences a steady decrease, falling to $\sim 103 \text{ mAh g}^{-1}$ by the 250th cycle. Our composite material shows higher overall capacity as well as capacity retention when compared to TiO_2 IOs and carbon IOs shown in Fig. 5d. The TiO_2 IO had an initial discharge and charge capacity of 343 and 162 mAh g^{-1} respectively, falling to 60.45 and 49.7 mAh g^{-1} for the final discharge and charge. While the carbon IOs showed 364 mAh g^{-1} for the first discharge with an ICE of 18%, falling to 65 mAh g^{-1} by the 10th cycle and failing before the 100th cycle. The C/TiO_2 material experienced a capacity loss of 68% from the 2nd to 250th cycle, excluding the first cycle because of SEI layer formation, while TiO_2 experienced 72% loss. This better performance at high rates may be due to the conductivity of carbon in our C/TiO_2 material.⁵⁹ While we do see relatively low coulombic efficiency for both materials, our C/TiO_2 possesses an average CE of 87.3% over the 250 cycles while the TiO_2 had an average CE was 80.7%.

The rate performances of C/TiO_2 , TiO_2 and carbon inverse opals at the current rates of $0.2 - 1.5 \text{ C}$ are compared in Fig. 6a. The C rates were calculated from the theoretical capacity of the composite material arising from the weight percentages, which equates to $\sim 70.4 \text{ wt\%}$ of carbon. The C/TiO_2 IO displayed good stability at high rates however, surprisingly, suffered greater capacity loss than its individual C and TiO_2 counterparts. Our composite material achieved average capacities of 461, 377, 325, 309, and 286 mAh g^{-1} for the 0.2, 0.5, 0.8, 1, and 1.5 C rates, respectively. This performance at high current density demonstrates that the incorporation of carbon enhances both cycling stability and high-rate performance when compared to TiO_2 IOs, under galvanostatic conditions. The TiO_2 IOs showed capacities of 244, 158, 131, 119 and 99 mAh g^{-1} for the same current densities, while carbon IOs achieved 393, 339, 274, 252, and 209 mAh g^{-1} , respectively. The reversible capacity of

C/TiO_2 IOs recovered to 403 mAh g^{-1} when the current density was reverted to 70 mA g^{-1} . This equates to a 12.8% loss in capacity after the specific current was returned to 0.2 C. This is similar, if not better, to rate performances observed in other C/TiO_2 macroporous structures, where capacity losses of 12%³¹ and 27%⁵⁷ were documented after rate tests. In comparison to the pure samples, TiO_2 IOs and carbon IOs lost 6.7% and 9.7% of their initial capacity, respectively, after the specific current was returned to the lower rate.

While the composite material exhibits lower capacity retention during the rate test compared to the individual carbon and TiO_2 IOs, an analysis of the charge/discharge curves at each specific current as shown in Fig. 6b, reveals that the composite material maintains a coulombic efficiency of $\sim 99\%$ when the current is returned to 0.2 C. Extended cycling at 70 mA g^{-1} for the C/TiO_2 IOs can be found in Fig. S5, along with the associated coulombic efficiencies.

Post-cycling structural characterization.—After electrochemical testing, the cells were disassembled for structural analysis using SEM to identify any changes resulting from cycling. Figure 7 shows line-scan profiles acquired from grey-scale SEM images of C/TiO_2 IO materials before and after cycling at current densities of 150 mA g^{-1} and 700 mA g^{-1} . These profiles clearly reveal the periodicity of the materials and illustrate the minimal volume expansion observed in the IO material post cycling. Specifically, after 250 cycles at 150 mA g^{-1} (Fig. 7a) there was a negligible change ($<1\%$ increase) in wall diameter.

Even at the higher rate of 700 mA g^{-1} , the samples retained their structural integrity, experiencing only a 19% volume expansion, with a pore diameter of $\sim 500 \text{ nm}$ for the pristine material to $\sim 405 \text{ nm}$ diameter for the same material after cycling. Several factors likely contribute to these outcomes. Firstly, the C/TiO_2 IO materials feature a substantial specific surface area and a network of interconnected pore structures. Consequently, the lithiation/delithiation process occurs within the porous channels as well as uniformly on the material surface, promoting the formation of stable SEI layers.^{60,61} Secondly, the honeycomb-like IO skeleton reduces the Li^+ transport resistance between the electrode and electrolyte.⁵⁶ Lastly, the carbon addition enhances the overall conductivity of TiO_2 , allowing the IO structure to serve as a continuous carrier for electron transport at higher rates under galvanostatic conditions where the voltage change is slow.

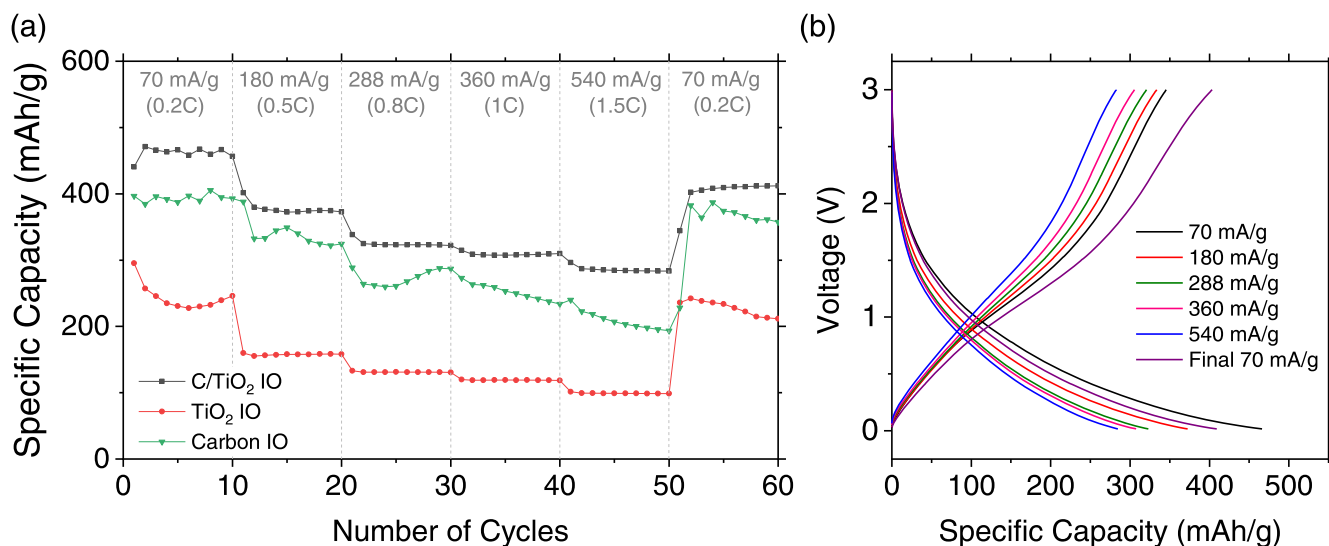


Figure 6. (a) Rate capability test for C/TiO_2 , pure TiO_2 and carbon inverse opals with various specific currents ranging from 70–540 mA g^{-1} . (b) Charge/Discharge curves for the 5th cycle of C/TiO_2 IOs at each current density in the rate test.

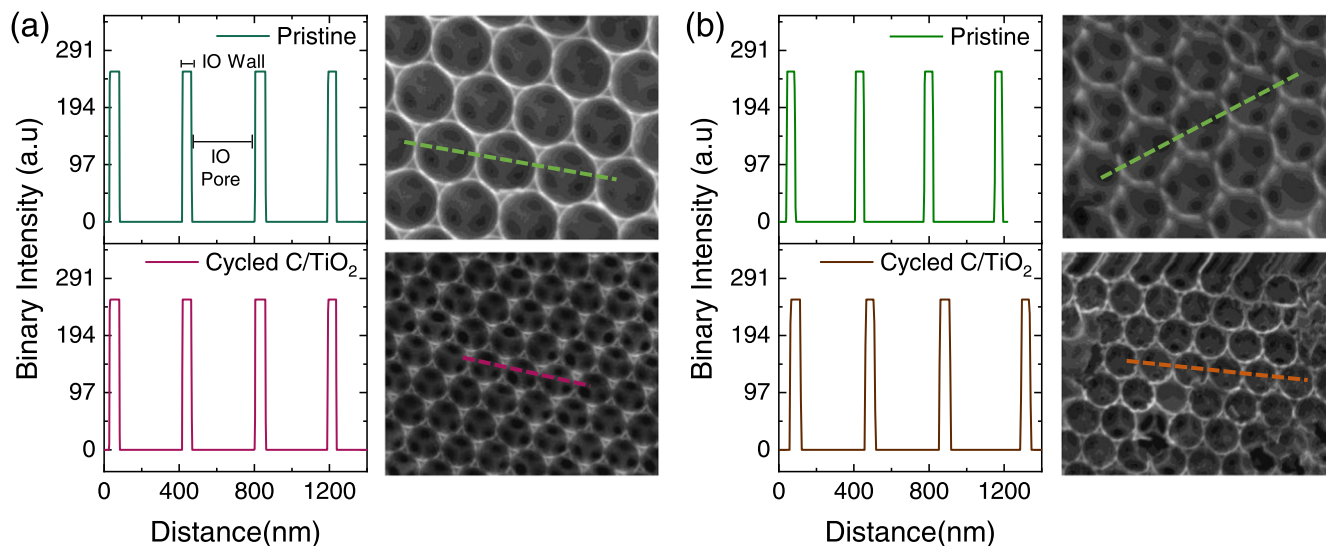


Figure 7. Line-scan profiles acquired from binary conversions of SEM images of C/TiO₂ IO anodes as prepared and after 250 cycles at (a) 150 mA g⁻¹ and (b) 700 mA g⁻¹.

Conclusions

Highly ordered, porous inverse opal structures can be made as C/TiO₂ nanocomposites using a facile method that involves a colloidal templating approach and sucrose as the carbon precursor. Material characterization showed amorphous TiO₂ at the atomic scale with 3D architecture at the macro scale. EDS shows uniform distribution of C, Ti and O elements.

The C/TiO₂ inverse opal electrodes exhibited high initial discharge and charge capacities of ~870 mAh g⁻¹ and 472 mAh g⁻¹, exceeding theoretical limits for TiO₂ and carbon. This enhanced performance could potentially be linked to defects formed during calcination, which provide additional charge compensation sites for lithium. The porous structure contributed to remarkable capacity retention and improved coulombic efficiency (99.6% after 250 cycles), outperforming the individual carbon and TiO₂ materials. Despite a 68% loss in capacity from the 2nd to 250th cycle at a high current density of 700 mA g⁻¹, C/TiO₂ maintained an average Coulombic efficiency of 87.3%, surpassing that of pure TiO₂ IO at ~81%. Rate testing further revealed our C/TiO₂ IO material's specific capacities when compared to both TiO₂ and carbon IOs at various specific currents. Despite experiencing greater capacity loss than the individual counterparts, C/TiO₂ maintained stable CE at all currents.

Post-mortem analysis shows our C/TiO₂ IOs maintain a high-quality inverse opal architecture after cycling, indicating minimal expansion (1% and 19%) after 250 cycles at 150 mA g⁻¹ and 700 mA g⁻¹, respectively. The electrochemical and physical properties of C/TiO₂ IOs are attributed to the ordered interconnected macroporous structure that can help with electrolyte wetting, increased surface area, interconnected pores which accommodate for volume expansion and reduce Li⁺ transport resistance. While capacitive effects from the composite are seen under voltammetric conditions at higher rates, slower scan rates and all galvanostatic measurements are primarily diffusion-limited and promote intercalation reactions. The data highlights some benefits of tailoring porous material and their compositions to improve capacity and rate-behavior.

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