Evidence for Fast Lithium-Ion Diffusion and Charge-Transfer Reactions in Amorphous TiO$_x$ Nanotubes: Insights for High-Rate Electrochemical Energy Storage

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Supporting Information

ABSTRACT: The charge-storage kinetics of amorphous TiO$_x$ nanotube electrodes formed by anodizing three-dimensional porous Ti scaffolds are reported. The resultant electrodes demonstrated not only superior storage capacities and rate capability to anatase TiO$_x$ nanotube electrodes but also improved areal capacities (324 μAh cm$^{-2}$ at 50 μA cm$^{-2}$ and 182 μAh cm$^{-2}$ at 5 mA cm$^{-2}$) and cycling stability (over 2000 cycles) over previously reported TiO$_x$ nanotube electrodes using planar current collectors. Amorphous TiO$_x$ exhibits very different electrochemical storage behavior from its anatase counterpart as the majority of its storage capacity can be attributed to capacitive-like processes with more than 74 and 95% relative contributions being attained at 0.05 and 1 mV s$^{-1}$, respectively. The kinetic analysis revealed that the insertion/extraction process of Li$^+$ in amorphous TiO$_x$ is significantly faster than in anatase structure and controlled by both solid-state diffusion and interfacial charge-transfer kinetics. It is concluded that the large capacitive contribution in amorphous TiO$_x$ originates from its highly defective and loosely packed structure and lack of long-range ordering, which facilitate not only a significantly faster Li$^+$ diffusion process (diffusion coefficients of 2 × 10$^{-14}$ to 3 × 10$^{-13}$ cm$^2$ s$^{-1}$) but also more facile interfacial charge-transfer kinetics than anatase TiO$_x$.

KEYWORDS: high-rate energy storage, lithium-ion battery, anode material, amorphous TiO$_x$ nanotubes, insertion kinetics, potentiostatic intermittent titration technique, lithium-ion diffusion

1. INTRODUCTION

High rate capability is becoming increasingly important for electrochemical energy storage required for electric vehicles and renewable power systems.$^{1-3}$ Lithium-ion batteries are considered as the most promising candidates for these applications because of their high energy densities, relatively long cycle lives, and technological maturity in the field of portable electronic devices.$^{1,5}$ Yet, challenges remain for them to retain a sufficient energy density, cycle life, and most importantly safe operation when they are charged/discharged at high rates. Enhancing the rate capability of electrode materials requires an understanding of the fundamental processes involved in charging and discharging so that rate-limiting steps can be addressed by systematic engineering. This investigation process is somewhat different from that typically adopted for the objective of increasing energy density, or capacity, where the more common approach is to seek new materials or material combinations that can achieve greater charge storage without significantly impacting cyclability.$^6$

Among many anode materials, titanium oxide (TiO$_x$) has demonstrated attractive features in terms of low cost, minimal solid electrolyte interphase formation and superior coulombic efficiencies and cycling stability$^7$ due to its excellent structural stability upon lithiation and delithiation with a limited volume change of <4%. More importantly, its high operating potential (ca. 1.5−1.7 V vs Li/Li$^+$) is well above the Li plating potential, making it a safer alternative to the state-of-the-art graphite electrode (lithiation potential at ~0.1 V vs Li/Li$^+$).$^5,7$ This characteristic is especially important for high-power devices since Li plating is more likely to occur at high charging/discharging rates.$^9$ In spite of all of the advantages, bulk TiO$_x$ suffers from the poor ionic and electronic conductivity.$^{10,11}$ To overcome these limitations, many studies have reported the use of nanostructured TiO$_x$ (e.g., nanoparticles, nanotubes, nanowires, and mesoporous structures)$^{11-12}$ or TiO$_2$-based composites$^{13-15}$ to achieve improved storage capacities and rate capabilities. In particular, self-supported and electrochemically grown TiO$_x$ nanotube (NT) electrodes have drawn significant attention because of their fabrication simplicity, large electrode/electrolyte surface area, short Li$^+$ diffusion path through the tube walls, and minimal structural changes during cycling.
The electrochemical performance (capacity, rate capability, and cyclability) and charge-storage mechanisms have been comprehensively studied for crystalline (anatase) TiO₂ (hereafter denoted as c-TiO₂) NT electrodes, and results suggest that a considerable fraction of the overall capacity in c-TiO₂ NTs arises from capacitive storage processes.²⁶,²⁷ Interestingly, several recent studies have found that amorphous TiO₂ (hereafter denoted as a-TiO₂) electrodes can achieve significantly higher capacities and rate capability than their crystalline counterparts.²⁸−³⁰ Despite these reports of enhanced performance, investigations on the origin of the enhanced rate in a-TiO₂ are limited. Xiong et al.³¹ identified capacitive processes for Li⁺ storage in a-TiO₂ using estimates of $b$-value³²,³³ obtained from cyclic voltammetry (CV) measurements. In a later article, the authors attributed the superior capacity and cyclability of a-TiO₂ to the possible atomic rearrangement in the amorphous material when discharged below ~1 V during the first cycle.³⁴ Although a detailed microscopic analysis was reported, the discussion on charge-storage kinetics in a-TiO₂ was limited to the simulation results. Han et al. further analyzed the diffusive and capacitive contributions of Li⁺ insertion in a-TiO₂ composite electrodes consisting of thin-film TiO₂ and graphene.³⁵ Despite the outstanding capacity and rate capability of 122 mAh g⁻¹ at 100 C being attained by the composite electrodes, the inclusion of graphene (an electric double-layer (EDL) capacitor material) can introduce uncertainties into the analysis of storage mechanism. In this paper, we have extended the kinetic analyses that have been previously reported for a-TiO₂ NT electrode and presented a more detailed investigation of the charge-storage kinetics in both a-TiO₂ and c-TiO₂ NT electrodes using a combination of electrochemical methods including scan-rate-dependent CV, potentiostatic intermittent titration technique (PITT), and electrochemical impedance spectroscopy (EIS) measurements. From this analysis, we obtained quantitative evidence to elucidate the distinct Li⁺-storage behavior and therefore the superior rate performance of a-TiO₂ compared to the crystalline form. The NT electrodes were fabricated by electrochemically growing TiO₂ NTs on the surface of three-dimensional (3D) porous Ti foams, the foams being utilized as current-collecting scaffolds. The self-supported structure of TiO₂ NTs on the foam eliminates the need for any binder or conductive additives, making the electrode an ideal system with which to study the active material’s fundamental electrochemical behavior. This study also highlights the potential advantages of using amorphous electrode materials for high-rate electrochemical storage and the need to increase the understanding of Li⁺ diffusion and charge-transfer reaction kinetics for these materials.

2. EXPERIMENTAL SECTION

2.1. X-ray Computed Tomography. The 3D micro X-ray computed tomography (CT) was performed using an 8 mm diameter disk of the Ti foam (TOB New Energy) to determine: (i) the open surface area, which is accessible to the electrolyte during anodization, and (ii) the pore size distribution of the foam. The CT images were acquired using a customized CT equipment (Tyerx X-ray CT facility, UNSW) with an excitation energy of 120 kV. A steel filter with a thickness of 3 mm was applied to remove the beam hardening and increase the signal contrast.

For quantitative analysis, the reconstructed 3D tomogram was used to determine the different phase materials by a semiautomatic segmentation approach.²⁶ After segmentation, Ti metal and pores were distinguished and the material defined image was then used to perform the surface density calculation. The open surface area was estimated through surface triangulation on the voxels neighboring Ti metal, and the percolation-type spanning cluster algorithm was employed to bound the calculations only to interconnected and thus accessible pore spaces. Uncertainties in the surface area estimation arose from the noise-to-signal boundary set for the segmentation procedure, the tomogram resolution (i.e., the number of voxels), and the discretization effects.²⁶ For the analysis in this study, we used tomograms with a 3D of 2520 × 2520 × 1320 voxels (at 4.59 μm voxel size). For the calculations of pore radius distribution, covering radius transform,²⁷ a method restricted to local pore morphology without considering the history of pore channels (e.g., throats), was performed and the pore size was estimated from the radius of the largest covering sphere in each voxel. Additional figures and details are provided in Supporting Information Figure S1.

2.2. Electrode Preparation. Titania NTs were grown electrochemically by a one-step anodization process. Prior to anodization, pure Ti foams were cleaned by ultrasonication in acetone, isopropanol, and deionized water for 10 min each. Titanium foams were immersed in the anodization electrolyte (0.45 M NH₄F and 2.5% v/v deionized water in glycerol) and placed in a vacuum environment for 40 min before anodization to ensure the access of electrolyte to the inner surface of the foams. Anodization was performed in a two-electrode configuration with the Ti foam serving as the anode and a platinized Ti plate being used as the cathode. The NTs were grown by applying a constant voltage of 35 V to the Ti foam for 50 min after a voltage ramp of 1 V s⁻¹. After anodization, the Ti foams were first rinsed with deionized water, then soaked sequentially in the mixture of 1:1, 2:3, 4:1 v/v ethanol/deionized water and pure ethanol for 5 min each, and finally dried in ambient air. To prepare crystalline electrodes, the as-anodized TiO₂ NTs electrodes were annealed at 400 °C for 1 h in air.

2.3. Material Characterization. Ex situ thin-film X-ray diffraction (XRD) was recorded in a PANalytical Empyrean diffractometer with Cu Kα emission ($\lambda = 1.5418$ Å). Raman spectroscopy was acquired using a Renishaw inVia spectrometer with a laser wavelength of 532 nm. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were conducted by an FEI Nova NanoSEM 450 FE-SEM microscope and a Phillips CM200 TEM microscope, respectively. Selected area electron diffraction (SAED) pattern was acquired by an FEI Tecnai G2 20 TEM microscope with an aperture diameter of ~200 nm. X-ray photoelectron spectroscopy (XPS) was conducted by Thermo Scientific UK ESCALAB250Xi under ultrahigh vacuum. The X-ray source was monochromated Al Kα (energy of 1486.68 eV) with the binding energy scale being calibrated using a carbon reference (C 1s = 284.8 eV).

2.4. Electrochemical Characterization. Electrochemical measurements were performed using R2032-type coin cells with TiO₂ NT electrodes serving as the anode and Li foils serving as the cathode. Prior to cell assembly, the as-anodized Ti foams were dried at 60 °C for 24 h to remove any residual solvent. A volume of 80 μL of 1 M LiPF₆ in a 1:1 v/v mixture of ethylene carbonate and ethyl methyl carbonate was used as electrolyte and battery-grade microporous membranes as separators. All coin cells were assembled in an Ar-filled glovebox and then characterized using an IviumStat.XR potentiostat (Ivium Technologies) in atmosphere at room temperature.

Galvanostatic charge and discharge (GCD) measurements were conducted at different current densities for a potential range of 1.0−3.0 V with respect to the Li/Li⁺ potential. These data were used to estimate the areal and specific capacity of TiO₂ NTs electrodes. The mass of the active material was estimated from the volume of TiO₂ NTs calculated using the SEM images and CT data and by assuming densities of 3.77 and 3.84 g cm⁻³ for the amorphous and anatase TiO₂, respectively.²⁹ CV curves were recorded at scan rates ranging from 0.05 to 100 mV s⁻¹ for the same potential range as the GCD measurements.
EIS and PITT measurements\textsuperscript{30,31} were performed after 90 CV cycles to ensure quasi-reversible conditions. Prior to EIS measurements, the test cells were discharged to 2 V from their open-circuit voltages to enable comparisons between different cells at the same voltage. The impedance spectra were acquired in a frequency range of 100 kHz to 10 mHz with an AC voltage amplitude of 10 mV. For PITT measurements, the working electrode was first set to 3 V and equilibrated for 500 s. This was followed by the application of a series of potential steps of $-25$ mV with 500 s equilibration time at each step until the working electrode potential reached the lower limit of 1 V. This process was reversed with a series of potential steps of $+25$ mV until the potential upper limit of 3 V was reached. The current response after each potential step was recorded with a data collection time step of 0.01 s.

2.5. Scan-Rate-Dependent CV and PITT Analysis. To distinguish quantitatively different storage mechanisms to the overall charge storage in TiO$_x$ electrodes, the current response $I(V)$ at a fixed potential was assumed to be a combination of capacitive (i.e., non-diffusion-controlled) $k_1\nu$ and diffusion-controlled processes $k_2\nu^{1/2}$:

$$I(V) = k_1\nu + k_2\nu^{1/2}$$  \hspace{1cm} (1)

where $k_1$ and $k_2$ are adjustable parameters. From the CV data, a graph of $I(V)/\nu^{1/2}$ as a function of $\nu^{1/2}$ was generated at each potential for scan rates between 0.05 and 100 mV s$^{-1}$. Then, $k_1$ and $k_2$ were determined from the slope and intercept of the linear fitting to each plot, respectively.

Specific capacities $Q$ of TiO$_x$ electrodes for the different charge-storage processes were estimated from CV curves at different scan rates by integrating their corresponding current $I(V)$ of the anodic half-cycle

$$Q = \frac{\int_{V_0}^{V_1} I(V) dV}{\nu m}$$  \hspace{1cm} (2)
where $V_0$ and $V_1$ define the voltage range for which current is positive, $m$ is the mass of active electrode material, and $v$ is the scan rate.

For the determination of the chemical diffusion coefficient of a guest species in a thin-film host material, a linear and restricted (blocking) diffusion model in which the diffusion flux is assumed to be zero at some distance $L$ from the electrolyte/electrode interface was used. Using this model, the transient current response from an electrode to a potential step, $I(t)$, is given by\(^1\)^\(^3\)^\(^4\)

$$I(t) = 2 \frac{\Delta Q}{\tau_0} \sum_{n=1}^{\infty} \exp \left( -2(n-1)^2 \frac{t^2}{4 \tau_0^2} \right)$$

where $t$ is the elapsed time from the start of the potential step. The diffusion time constant $\tau_0$ and the amount of faradic charge passed during the process $\Delta Q$ are defined by

$$\tau_0 = L^2 / D, \quad \Delta Q = \int_0^\infty I(t) dt = -FA\Lambda \Delta c$$

where $L$ is the diffusion length, $D$ is the chemical diffusion coefficient of the guest species, $F$ is the Faraday constant, $\Lambda$ is the electrochemically active surface area, and $\Delta c$ is the change of guest species concentration in the host material due to the applied potential step. This model assumes that the insertion reaction of the guest species in host material is solely governed by a diffusion process (i.e., very fast charge-transfer kinetics with negligible Ohmic potential drop and EDL charging current).

However, as already discussed in a number of reports,\(^3\)^\(^4\)^\(^5\)^\(^6\) application of this model to insertion materials, which exhibit slow charge-transfer kinetics and/or non-negligible Ohmic resistance, can result in erroneous estimates for diffusion coefficients. In this study, we employed the model reported by Montella\(^4\) to analyze Li$^+$ insertion in a-TiO$_2$ and c-TiO$_2$ host materials. This model assumes an insertion process under the mixed control of: (i) linear restricted diffusion; (ii) charge-transfer kinetics at electrode/electrolyte and electrode/current collector interface; and (iii) Ohmic potential drop. Using this model, the current response $I(t)$ to a small potential step can be expressed as

$$I(t) = 2 \frac{\Delta Q}{\tau_0} \sum_{n=1}^{\infty} \frac{\Lambda^2}{\Lambda^2 + \Lambda + b_n^2} \exp \left( -b_n^2 \frac{t^2}{4 \tau_0^2} \right)$$

where $b_n$ is the $n$th positive root of the equation

$$b \tan b - \Lambda = 0$$

The dimensionless parameter $\Lambda$ provides a measure of the relative contributions of diffusion and other rate-limiting processes

$$\Lambda = \frac{R_d}{R_d + R_{ct}}$$

where $R_d$ is the diffusion resistance, $R_{ct}$ is the Ohmic resistance, and $R_{ct}$ is the interfacial charge-transfer resistance. It should be noted that this kinetic model also assumes that the contribution of EDL charging current is small compared to the total current. The validity of this assumption is discussed further in the Results and Discussion section.

After each potential step, the transient current $I(t)$ was recorded and eq 5 was fitted to the data using nonlinear least-squares regression, with $\Lambda$, $\tau_0$, and $\Delta Q$ being treated as fitting parameters. To ensure fair contributions from data in different time domains, the measured data were interpolated to a fixed number of equidistant points on a log($t$) scale and this data set was used for the curve fitting procedure. The initial guess of $\Delta Q$ was estimated from the integral of current transient $I(t)$ with respect to $t$. The summation term in eq 5 was iterated until the $n$th term was less than $10^{-6}$ of the sum of previous terms. Given that Li$^+$ diffusion in the electrolyte is typically orders of magnitude faster than in solid-state host materials\(^1\)^\(^9\) and the specific capacities of TiO$_2$ NT electrodes have been found to be independent of the tube length (at least for tube length <3.8 $\mu$m),\(^10\) it was assumed that transport of Li$^+$ into the inner- and internanotube voids readily occurs and Li$^+$ insertion/extraction can occur homogeneously across the entire length of a nanotube and symmetrically from both sides of the tube wall. Therefore, in the calculations of Li$^+$ diffusion coefficients in host TiO$_2$ NTs, symmetrical linear diffusion was assumed, and the diffusion length $L$ in eq 4 was assumed to be 1/2 of the wall thickness of TiO$_2$ NTs (Figure 1e). The goodness of fit was evaluated using an R-square analysis, and additional details are provided in Supporting Information Figure S5.

3. RESULTS AND DISCUSSION

The 3D porous Ti foam scaffolds provided an interconnected metallic network for electron transport while also facilitating electrolyte access to the inner and outer surfaces of the foam (Figure 1a,d). The open surface area (i.e., surface area accessible to electrolyte) and porosity of the foams used were computed to be 14.6 $\text{mm}^2$ per $\text{mm}^3$ and ~25%, respectively, from the X-ray CT analysis. Approximately 83% of the pores were estimated to have an equivalent radius between 25 and 100 $\mu$m, ~16% to have a radius <25 $\mu$m and ~1% to have a radius >100 $\mu$m (see Figure S1d). Self-supported TiO$_2$ NTs were grown on both the outer and inner surfaces of the foams during the anodization process (Figure S2). The rough initial surface of the Ti foam provided for strong adhesion of the self-supported TiO$_2$ NTs to the Ti surface and therefore good electrical contact between the TiO$_2$ and the Ti of the scaffold. This eliminated the need for any binders and conductive additives.

The as-grown TiO$_2$ NTs had an average outer diameter of 60.2 ± 3.4 nm and a tube length of 2.4 ± 0.1 $\mu$m, as shown in Figure 1b and Table 1. Assuming the geometry of TiO$_2$ NTs shown in the SEM images and a homogeneous cover of TiO$_2$ NTs on the entire open surface area of the Ti foam, the specific surface area was estimated to be 73.1 $\text{m}^2\text{g}^{-1}$. This represents a significant increase over the specific surface area of TiO$_2$ NTs grown on planar Ti foils (24–28 $\text{m}^2\text{g}^{-1}$\(^5\)\(^8\) and 38–47 $\text{m}^2\text{g}^{-1}$\(^9\)^\(^10\)). A mass loading of 2.4 mg cm$^{-2}$ (per electrode projection area) was calculated for the TiO$_2$ film thickness (i.e., NT length) of 2.4 $\mu$m. The TEM image of an NT before annealing (Figure 1e) showed no lattice fringes, and the SAED (Figure 1e inset) was featureless, indicating that the as-grown TiO$_2$ NTs were amorphous (at least long order of lattice structure was absent), which is in agreement with previous reports.\(^9\)^\(^10\) The XRD spectrum (Figure 1g) confirmed the
amorphous form of the as-grown TiO$_x$ NTs (so hereafter denoted as a-TiO$_x$) with the only evident peaks corresponding to Ti metal. The Raman spectrum (Figure 1h) of a-TiO$_x$ showed very weak and broad peaks (distinct from the flat line for the Ti foam) suggesting the presence of some short-range local ordering in the a-TiO$_x$. After annealing, no significant changes in the morphology of TiO$_x$ NTs were observed (Figure 1c); however, lattice fringes were evident in the TEM image (Figure 1f) and the SAED diffraction rings (Figure 1f, inset) corresponded to the d-spacing of polycrystalline anatase TiO$_2$ (I4$_1$/amd). The anatase phase of the annealed TiO$_x$ NTs was also confirmed by XRD patterns (Figure 1g) and Raman spectra (Figure 1h), so hereafter we denote this electrode as c-TiO$_x$. Chemical composition of TiO$_x$ NTs was investigated using XPS. The measured Ti 2p core-level spectra of a-TiO$_x$ and c-TiO$_x$ (Figure S6a) showed two distinct peaks at binding energies of 464.4 and 458.8 eV, respectively, which are close to the typical values reported for the 2p$_{1/2}$ and 2p$_{3/2}$ doublet of Ti$^{4+}$, suggesting that the surface films of both a-TiO$_x$ and c-TiO$_x$ electrodes were stoichiometric TiO$_2$. However, stoichiometry of the film interiors is difficult to be determined accurately using XPS as the oxidation state of Ti can be affected by sputtering, a process typically used in the depth profiling analysis to etch the film surface.

The a-TiO$_x$ and c-TiO$_x$ electrodes were each combined with a Li foil electrode and assembled into coin cells to assess their electrochemical performance. Figure 2a,b shows the GCD curves of the a-TiO$_x$ and c-TiO$_x$ electrodes for Li$^+$ insertion/extraction at C-rates between 0.125 C and 12.5 C (the 1 C value was defined as 168 mA g$^{-1}$ corresponding to 1 h charge/discharge current of a theoretical capacity of 168 mAh g$^{-1}$, which assumes a stoichiometry of 0.5 Li per TiO$_2$ formula unit$^{[6,23,42]}$). The c-TiO$_x$ electrode (Figure 2b) exhibited plateaus at $\sim$1.75 and $\sim$1.9 V in the lithiation and delithiation curves, respectively. These correspond to a phase transition between the Li-poor Li$_x$TiO$_2$ ($0.01 < x \leq 0.21$) with tetragonal anatase structure (I4$_1$/amd) to the orthorhombic Li-titane (Li$_{0.55}$TiO$_2$) phase (Imma)$^{[43]}$. The phase transitions are in good agreement with those reported for anatase TiO$_2$ electrodes in the literature.$^{[16,19,29,44]}$ In addition to the main plateaus, an additional pair of plateaus, observed at $\sim$1.46 V (lithiation) and $\sim$1.73 V (delithiation), are indicative of a second-phase transition to a fully lithiated Li$_x$TiO$_2$ (I4$_1$/amd), which typically occurs in TiO$_x$ crystallites with size $< 7$ nm.$^{[43,45]}$ In contrast, no plateaus were present in the lithiation/delithiation curves of the a-TiO$_x$ electrode and the voltage varied almost linearly with capacity, indicating a capacitive-like storage behavior.$^{[46]}$

The specific capacities of the a-TiO$_x$ and c-TiO$_x$ electrodes at different C-rates were calculated from the GCD measurements (see Figure 2c). The a-TiO$_x$ electrode demonstrated superior specific capacity and rate capability to the c-TiO$_x$ electrode, achieving $\sim$135 mAh g$^{-1}$ at 0.125 C (21 mA g$^{-1}$) and 77 mAh g$^{-1}$ (i.e., 56% capacity retention) at 12.5 C (2106 mA g$^{-1}$) in contrast to $\sim$102 mAh g$^{-1}$ at 0.125 C and 28 mAh g$^{-1}$ at 12.5 C (i.e., 27% capacity retention) being attained by the c-TiO$_x$ electrode. Such specific capacities are slightly lower than the previously reported values for electrochemically grown a-TiO$_x$ and c-TiO$_x$ NT electrodes (see Table S1). The slightly lower values may be due to an overestimation of the active material mass (leading to an underestimation of the electrode specific capacities) as the lengths of TiO$_x$ nanotubes grown on the outer surface of a Ti foam were used in the material mass calculation; however, shorter nanotubes were observed on the inner foam surfaces presumably due to a limited access of electrolyte within the deeper pores of the foam during anodization. On the other hand, the areal capacities of the a-TiO$_x$ electrode achieved in this study (calculated using the projection area of the electrode), 324 $\mu$Ah cm$^{-2}$ at 50 $\mu$A cm$^{-2}$ and 182 $\mu$Ah cm$^{-2}$ at 5 mA cm$^{-2}$, represent a significant increase over the corresponding previously reported values, 68−200 $\mu$Ah cm$^{-2}$ at 5−10 $\mu$A cm$^{-2}$ and 30−115 $\mu$Ah cm$^{-2}$ at 0.1−0.5 mA cm$^{-2}$.$^{[39,41,47]}$ (see Supporting Information Figure S3 and Table S2 for details). The improved areal capacities at both low and high rates were presumably due to the large electrode surface area realized by using the 3D porous Ti foams as current-collecting scaffolds. This ensures a larger per-area mass loading of active material (higher areal capacities) without significant increases in the a-TiO$_x$ film thickness, leading to an improved rate capability. The a-TiO$_x$ electrodes demonstrated excellent cycling stability, attaining a capacity retention of 92% (108 mAh g$^{-1}$) after 2000 cycles and Coulombic efficiencies of 99.9 ± 0.15% in comparison to 80% (71 mAh g$^{-1}$) and 100 ± 0.29% for the c-TiO$_x$ electrodes (Figure 2d).

Figure 3a,b shows the results of CV measurements between 0 and 3 V vs Li/Li$^+$ with scan rates ranging from 0.05 to 100 mV s$^{-1}$ for the a-TiO$_x$ and c-TiO$_x$ electrodes, respectively. For
the c-TiO\textsubscript{x} electrode, two pairs of sharp peaks were distinct in the CV curves, i.e., main peaks at 1.73/2.0 V and small peaks at 1.46/1.7 V, which are in good agreement with the plateau positions identified in the GCD curves. Such sharp peaks were absent in the CV curves for the a-TiO\textsubscript{x} electrode, and instead, two broad humps over a large range of potentials were evident. This CV response was previously ascribed to the nonuniform distribution of free spaces in the highly disordered and defective structures of the a-TiO\textsubscript{x} material, resulting in a broad potential range for Li\textsuperscript+ insertion/extraction.\textsuperscript{19,48}

To understand the reasons why a-TiO\textsubscript{x} electrodes have improved storage capacities and rate capability than c-TiO\textsubscript{x} electrodes, the scan-rate-dependent CV data were analyzed and the \textit{b}-values were determined from the anodic peak current \textit{I}_\text{p} in CV curves at various scan rates \textit{\nu} according to\textsuperscript{22,23}

\begin{equation}
\textit{I}_\text{p} \text{=} \textit{a\nu}^\text{b}
\end{equation}

where \textit{a} and \textit{b} are adjustable parameters. Figure 3c depicts the log \textit{I}_\text{p} vs log \textit{\nu} plots for the a-TiO\textsubscript{x} and c-TiO\textsubscript{x} electrodes and the fitted lines to the measured data, from which the slopes were used to determine the \textit{b}-values for both electrodes. A \textit{b}-value of 0.5 indicates a diffusion-controlled process, whereas a value of 1 implies a capacitive storage process.\textsuperscript{32} It worth clarifying that, although termed as “capacitive”, the capacitive component in this study is the sum of any non-diffusion-controlled contributions, which includes EDL storage,\textsuperscript{49} surface pseudocapacitive storage,\textsuperscript{50} and/or bulk-insertion pseudocapacitive storage.\textsuperscript{51,52} For scan rates between 0.05 and 2 mV s\textsuperscript{-1}, the \textit{b}-value for the c-TiO\textsubscript{x} electrode was estimated to be 0.50, suggesting a diffusion-controlled Li\textsuperscript+ insertion/extraction process in c-TiO\textsubscript{x}. In contrast, the a-TiO\textsubscript{x} electrode showed a \textit{b}-value of 0.96, indicating that Li\textsuperscript+ storage in its structure was predominantly capacitive. Unfortunately, the log \textit{I}_\text{p} vs log \textit{\nu} plots for both electrodes deviate from the linear model at scan rates >2 mV s\textsuperscript{-1}, making it unreliable to analyze charge-storage mechanisms at higher scan rates.

By employing the approach reported by Liu et al.,\textsuperscript{32} the diffusion-controlled and capacitive contributions to the current in CV curves for a-TiO\textsubscript{x} electrode were quantitatively separated and are shown in Figure 3d. Results suggest that, in a-TiO\textsubscript{x}, the capacitive contribution dominates the overall charge storage over the entire investigation potential range even when cycling at low scan rates of 0.05 and 1 mV s\textsuperscript{-1} (corresponding to 22 and 1 h round-trip cycles). On the basis of these results, specific capacities due to the different charge-storage processes were determined and are shown in Figure 3f. Specific capacities of the capacitive contribution retain their initial values for scan rates of 0.05–1 mV s\textsuperscript{-1}, whereas the values of diffusive contribution decrease rapidly with increasing scan rates as expected. This resulted in a fractional increase of capacitive capacity from 79.2% at 0.05 mV s\textsuperscript{-1} to 95.4% at 1 mV s\textsuperscript{-1} in the a-TiO\textsubscript{x} electrode. Considering that the morphology of NTs and therefore the electrode surface area are similar between the a-TiO\textsubscript{x} and c-TiO\textsubscript{x} electrodes (see Figure 1b,c), differences in their electrochemical storage behavior suggested by the \textit{b}-value analysis cannot be solely
explained by surface-storage processes (i.e., EDL and surface pseudocapacitive storage). In fact, a recent investigation reported that, in a-TiO$_x$, a part of this capacitive storage behavior was realized in the bulk material and consequently has been attributed to insertion pseudocapacitive storage. It should be noted that, although analysis using scan-rate-dependent CV has been widely adopted to differentiate the contributions of the different storage mechanisms, linear fitting to the proposed model is not always valid and is often limited to a small scan rate range. In our material system (a-TiO$_x$), as depicted in Figure 3e, linear fitting to the measured data is only possible for low scan rates, restricting the validity of our analysis up to 1 mV s$^{-1}$ (results obtained for c-TiO$_x$ electrode are not physically meaningful due to its apparent peak shifting even in the small scan rate range, see Figure S4).

We used the PITT measurement analysis to elucidate the origin of the high fraction of capacitive storage in a-TiO$_x$ in contrast to its c-TiO$_x$ counterpart. Figure 4a shows the recorded current response of the a-TiO$_x$ electrode after each potential step. As an example, Figure 4b,c depicts in linear and logarithmic scales, respectively, the measured current at the potential of 1.5 V. The solid curves represent the nonlinear least-squares fit to the measurement data using eq 3 (pure diffusion-controlled insertion process; blue curve) and eqs 5 and 6 (mixed-controlled process; orange curve). Assuming a pure diffusion-controlled insertion process clearly overestimated the current response to the potential step in the short-time domain (<5 s) and underestimated the response in the long-time domain (>50 s). The model deficiency is more clearly illustrated in the logarithmic scale, in which a pure diffusion process should follow the Cottrell relation in the short-time domain with a slope of 0.5.

The measured current is more accurately described by Montella’s mixed-controlled model (eqs 5 and 6) in both short- and long-time domains, suggesting that Li$^+$ insertion/extraction in a-TiO$_x$ is not solely governed by solid-state diffusion in host structures, but rather the interfacial charge-transfer kinetics and Ohmic potential drop also contribute to limiting rate at which charge can be stored. By performing similar curve fitting using eqs 5 and 6 to the current transients after each potential step, the chemical diffusion coefficients $D$ of Li$^+$ in a-TiO$_x$ and c-TiO$_x$ were determined and are graphed in Figure 4d as a function of potential vs Li/Li$^+$. It should be noted that current transients measured at potentials at which phase transitions occur in the material (corresponding to CV peak positions) cannot be described adequately by eq 5 and therefore the $D$ values estimated for the c-TiO$_x$ electrode in these regions were omitted (shaded area in Figure 4d). Considering that the surface-area-normalized EDL capacitance was typically in the range of 2–20 μF cm$^{-2}$, the estimated surface area of 73.1 m$^2$ g$^{-1}$ (Table 1) for the a-TiO$_x$ electrode would result in an EDL capacity of 0.8–8.0 mAh g$^{-1}$, which represented a small proportion to the overall capacity of the a-TiO$_x$ electrode (77–135 mAh g$^{-1}$). This again proves the validity of the mixed-controlled model, as one assumption made by this model is that the contribution of EDL charging current is small compared to the total current.

The estimated $D$ values for c-TiO$_x$ are in the ranges of $7.7 \times 10^{-16}$ to $1.8 \times 10^{-15}$ and $9.2 \times 10^{-16}$ to $3.9 \times 10^{-15}$ cm$^2$ s$^{-1}$ for Li$^+$ insertion and extraction, respectively. These values are consistent with previously reported values. In contrast, the $D$ values for a-TiO$_x$ are $3.1 \times 10^{-14}$ to $3.4 \times 10^{-13}$ cm$^2$ s$^{-1}$ for Li$^+$ insertion and $2.2 \times 10^{-14}$ to $3.0 \times 10^{-13}$ cm$^2$ s$^{-1}$ for Li$^+$ extraction, almost 2 orders of magnitude larger than those for c-TiO$_x$, implying that Li$^+$ diffusion in a-TiO$_x$ is significantly faster than in c-TiO$_x$. This is likely due to crystallographic differences inherent in a-TiO$_x$ and c-TiO$_x$. The absence of long-range ordering (Figure 1g,h) and the loosely packed structure of a-TiO$_x$ can provide more free space and open spatial channels than available in c-TiO$_x$ (anatase), and therefore enable a facile diffusion pathway of Li$^+$ in its host structure.

The parameter $\Lambda$, defined as the ratio of $R_d$ to the sum of $R_{oh}$ and $R_d$ (eq 7), provides a measure of the relative contributions of diffusion and other rate-limiting processes. A large $\Lambda$ value is characteristic of a diffusion-controlled process, whereas a small $\Lambda$ value indicates a charge-transfer kinetically limited process and/or non-negligible Ohmic resistance. The large $\Lambda$ values in the order of $10^2$–$10^3$ for c-TiO$_x$ indicate that solid-state diffusion of Li$^+$ is the rate-limiting step, which confirms the results suggested by the $b$-value of 0.50 (see Figure 3c). Except for potentials >2.75 V, the $\Lambda$ values of 1–10 for a-TiO$_x$ are
substantially smaller suggesting a mixed-controlled insertion process, provided that the series resistances $R_d$ between the two electrodes are comparable as discussed later.

The solid-state diffusion of Li$^+$ in $a$-TiO$_x$ is sufficiently fast that its diffusion rate becomes competitive with the rate of charge transfer at the interface. Therefore, in the host structure of $a$-TiO$_x$, both processes control the rate of Li$^+$ insertion/extraction and this explains the high fraction of non-diffusion-controlled contributions in $a$-TiO$_x$ electrodes. The limiting of the charging/discharging rates of LIBs by the kinetics of charge-transfer reactions has also been observed for (crystal-line) LiFePO$_4$, one of the most intensively studied LIB cathode materials, by Bai and Bazant.$^{62}$ For LiFePO$_4$, the kinetics of charge storage were able to be remarkably enhanced by carbon coating of the metal oxide to increase electronic conductivity,$^{62,63}$ however, many recent reports also highlighted the importance of the minimizing reorganizational energy of the Li$^+$ at the electrolyte interface and suggested that higher rates may be achieved with 3D semiconducting electrodes.$^{64}$ These reports highlight the importance of addressing limitations with regard to the charge-transfer kinetics if high-rate energy storage is to be achieved practically.

To validate the results from the PITT analysis, EIS measurements were performed for each of the $a$-TiO$_x$ and $c$-TiO$_x$ electrodes at a potential of 2 V. Figure 5 depicts the Nyquist plots of the $a$-TiO$_x$ and $c$-TiO$_x$ electrodes showing measured data and best fitted curves (solid lines) from equivalent circuit models shown in the inset: $R_d$ is the electrolyte resistance, $R_{ct}$ is the interfacial charge-transfer resistance, CPE is a constant phase element modeling the EDL capacitance at the electrode/electrolyte interface, $Z_m$ is the finite-length Warburg element, and $C_{int}$ is the differential intercalation capacitance. Fitted values for the key circuit elements are summarized in the table (see Table S3 for all parameters).

Figure 5. Nyquist plots of the $a$-TiO$_x$ and $c$-TiO$_x$ electrodes showing measured data and best fitted curves (solid lines) from equivalent circuit models shown in the inset: $R_d$ is the electrolyte resistance, $R_{ct}$ is the interfacial charge-transfer resistance, CPE is a constant phase element modeling the EDL capacitance at the electrode/electrolyte interface, $Z_m$ is the finite-length Warburg element, and $C_{int}$ is the differential intercalation capacitance. Fitted values for the key circuit elements are summarized in the table (see Table S3 for all parameters).

Nyquist plots of both electrodes with symbols representing the measured data and lines showing the best fits by using the equivalent circuit depicted in the inset of Figure 5. In the equivalent circuit, $R_d$ is the electrolyte resistance, $R_{ct}$ is the charge-transfer resistance, and a constant phase element (CPE)$^{59,60}$ was used to model the EDL capacitance at the electrode/electrolyte interface. The low-frequency data were simulated by the Frumkin and Melik-Gaykazyan impedance,$^{59,64,67,68}$ which is equivalent to a finite-length Warburg element, $Z_m$,$^69$ in series with a differential intercalation capacitance, $C_{int}$ representing, respectively, the solid-state diffusion of Li$^+$ and the accumulation/consumption step of Li$^+$ in the host material. Modeling impedance spectra using equivalent circuits alone, without adequate understanding of the materials system and structure, can raise the problem of ambiguity. In our analysis, it was noted that multiple combinations of $R_d$ and $D$ values can represent the same set of experimental data. Therefore, we fixed diffusion resistance $R_d$ as an input parameter using the value estimated from the $\Lambda$ (see eq 7) to determine the diffusion coefficient $D$. The resulting parameters for the key circuit elements are reported in the table in Figure 5 (see Table S3 for parameters of all circuit elements).

The fitting resulted in $D$ values of $2 \times 10^{-14}$ and $3 \times 10^{-16}$ cm$^2$ s$^{-1}$ for the $a$-TiO$_x$ and $c$-TiO$_x$ electrodes, respectively. These estimates are consistent with the values obtained from the PITT analysis at the same potential ($4 \times 10^{-14}$ cm$^2$ s$^{-1}$ for $a$-TiO$_x$ and $1 \times 10^{-15}$ cm$^2$ s$^{-1}$ for $c$-TiO$_x$). Remarkably, although the series resistance $R_d$ values were comparable for the two electrodes, the charge-transfer resistance $R_{ct}$ of $a$-TiO$_x$ (29 $\Omega$) was significantly lower than that of $c$-TiO$_x$ electrode (78 $\Omega$). This suggests that not only is Li$^+$ diffusion faster in the $a$-TiO$_x$ electrode than in the $c$-TiO$_x$ electrode, but also the interfacial charge transfer may occur more rapidly in the amorphous material further contributing to its superior storage capacities and rate capability than the $c$-TiO$_x$ electrodes. One possibility is that Li$^+$ can ’enter’ the $a$-TiO$_x$ over the entire surface exposed to the electrolyte while, for $c$-TiO$_x$, ions need to diffuse laterally across the crystalline surface before their position coincides with a crystal channel into which the ions can diffuse. The surface of anatase TiO$_2$ is anisotropic, and Li$^+$ insertion and diffusion is more facile along the [001] direction.$^{64}$ Figure 1f suggests that the $c$-TiO$_x$ NTs were highly polycrystalline in structure with many different grain orientations. This would imply that nonpreferential crystal planes (other than (004)) may be exposed on the NT surface. Kang and Ceder reported enhanced charging/discharging rates for LiFePO$_4$ electrodes by coating crystalline LiFePO$_4$ micrometer-sized particles with an amorphous film.$^70$ They attributed the higher rate to faster transport of Li$^+$ to the preferential (010) facets from which they can be inserted in the metal oxide matrix.

4. CONCLUSIONS

The capacity and rate capability of $a$-TiO$_x$ and $c$-TiO$_x$ NT electrodes, formed by anodizing porous Ti foam current collectors, were analyzed and compared in this study. The Ti foam provided an interconnected metallic network for electron transport and a large open surface area of 14.6 mm$^2$ per mm$^3$, which ensured a high per-area mass loading of the active material without significantly compromising the electrode rate capability. The $a$-TiO$_x$/Ti foam electrode demonstrated superior specific capacities ($\sim 135$ mA g$^{-1}$ at 0.125 C and 77 mA g$^{-1}$ at 12.5 C) and rate capability (56% capacity retention) than its anatase counterpart (27% capacity retention). The achieved areal capacities of 324 $\mu$Ah cm$^{-2}$ at 50 $\mu$A cm$^{-2}$ and 182 $\mu$Ah cm$^{-2}$ at 5 mA cm$^{-2}$ and excellent cycling stability over 2000 cycles represented a significant improvement over many previously reported TiO$_2$ NTs electrodes utilizing planar foils.

Scan-rate-dependent CV analysis resulted in a $b$-value of 0.96 for the $a$-TiO$_x$ electrode and suggested that capacitive contributions dominated its overall storage capacities even at low scan rates (95.4% at 1 mV s$^{-1}$). The kinetic analysis
revealed that the diffusion coefficient of Li+ in the a-TiO2 NT electrode \((2 \times 10^{-14} \text{ to } 3 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1})\) was almost 2 orders of magnitude larger than that estimated for the c-TiO2 electrode. This faster diffusion of Li+ resulted in the insertion/extraction of Li+ in a-TiO2 being more appropriately described by a mixed-controlled process, with the rate not being purely limited by solid-state diffusion. Interestingly, the value of \(R_{CT}\) estimated for the a-TiO2 \((29 \Omega)\) was also significantly less than that for c-TiO2 \((78 \Omega)\), highlighting that not only do the Li+ diffuse more rapidly in the amorphous material, but the rate of the charge-transfer reaction is also higher. This superior rate capability of a-TiO2 was attributed to its highly defective structure, loose atomic packing, and lack of long-range ordering. This study also highlights the importance of identifying the key rate-limiting processes at an electrode surface if the rate capability of electrode materials is to be enhanced.

**ASSOCIATED CONTENT**

1. Supporting Information
   The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b16994.
   CT tomograms and pore size distribution; additional SEM and TEM images of TiO2 nanotubes/Ti foam; areal rate capability and cycling stability measurements; charge-storage mechanism analysis of c-TiO2 electrodes; R-square values for the fitting of PITT data; XPS Ti 2p and O 1s core-level spectra; and electrochemical performance of TiO2 nanotube electrodes previously reported in the literature (PDF)

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**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**
This work was supported by the Australian Research Council through Discovery Grant DP170103219 “Advanced Electrochemical Capacitors.” The first author acknowledges the Australian Government Research Program for providing the PhD scholarship. The authors thank Dr. Ji-Youn Arns and Prof. Christoph H. Arns for the acquisition and analysis of the X-ray CT images, and Yicong Hu for the acquisition of TEM images.

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