

Unveiling Facet-Dependent Interfacial Chemistry and Kinetics in Nanostructured Anatase TiO₂ for Li⁺ Storage

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Abstract

Titanium dioxide (TiO₂), while being an affordable and stable anode material for Li-ion batteries, suffers from limited Li⁺ insertion kinetics. To overcome this, we comprehensively investigate the facet-dependent electrochemical dynamics by synthesizing three distinct single-crystal anatase TiO₂ morphologies-cubic, truncated, and octahedral-with controlled exposure of {001}, {100}, and {101} facets. Combined electrochemical characterizations, rate testing, diffusion-coefficient analysis, impedance spectroscopy and post-cycling structural probes, reveal that morphologies enriched in high-energy {001} and {100} facets -cubic and truncated- show enhanced reversible capacity retention and higher effective Li⁺ diffusion coefficients compared with octahedral particles dominated by {101} facets. We show these improvements arise from surface stabilization and less parasitic reactions. Beyond titania, the work establishes a transferable, materials-centric approach, facet-controlled synthesis coupled with multimodal electrochemical and structural interrogation, for isolating and understanding structure–transport relationships in any emerging electrode materials. These mechanistic insights reframe facet engineering as an active strategy for designing high-rate, long-life intercalation electrodes.

1. Introduction

In recent years, the demand for high-performance batteries has surged due to the rapid development of portable electronics and electric vehicles. Extensive research has focused on enhancing lithium-ion batteries, recognized as the most promising energy storage technology, by exploring nanostructured materials such as stable transition metal oxides for improved safety, energy and power density, and cycle life.¹

TiO₂, known for its affordability, safety (high Ti^{4+/3+} redox potential), and high stability, has been extensively studied as an anode material for Li-ion batteries. Its Li⁺ insertion potential above 1.0V vs. Li/Li⁺ benefits the stability of the electrolyte and prevents decomposition and continuous growth of the Solid Electrolyte Interface (SEI). However, low electronic conductivities and the constrained Li⁺ insertion into the TiO₂ structure are major drawbacks of this structure.² Lots of effort has been dedicated to enhancing the limited solid-state diffusion kinetics which makes the electrochemical characteristics notably influenced by factors such as crystallographic structure, particle size, and morphology³.

Anatase, rutile, and bronze are the popular crystallographic structures of titania capable of accommodating Li⁺. The micron-sized particles of these phases show very low Li⁺ inclusion ($\sim \text{Li}_{0.08}\text{TiO}_2$)^{4, 5}, which is far less than theoretical lithiation of TiO₂ structure. By reducing the particle size⁶, growing arrays⁷, and fabrication of electrospun electrodes^{8, 9}, the capacity improves in line with extensive exposure of active materials to the electrolyte. Sol-gel¹⁰, anodic oxidation^{7, 11}, template-assisted^{12, 13}, and hydrothermal treatments^{14, 15} are examples of the methods for developing nanostructured TiO₂ particles with a variety of morphologies aiming to improve Li⁺ intercalation kinetics and storage (up to $\text{Li}_{0.8}\text{TiO}_2$)¹⁶. Moreover, controlling the morphology of the nanostructures showed improvement in performance by exposing certain facets for Li⁺ insertion¹⁷⁻¹⁹.

All these methods aim to achieve high quality, uniform, and specific morphologies with minimum possible steps. Hydrothermal treatment is capable of synthesizing nanoparticles with desired shape and size by practicing control over capping agent, temperature, duration, environment, and pressure²⁰. One of the popular routes of TiO₂ nanoparticle synthesis is using the commercially available titania powders to grow sodium titanate nanotubes under alkaline conditions^{8, 21, 22}. The achieved nanotubes are then used as a precursor to synthesize various titania morphologies assisted by different shape-capping agents²³.

The shape capping agents reduce the surface energy of the TiO₂ nanoparticles and allow the creation of new facets in the nanostructure which are unstable in the lack of shape capping agents²⁴. By employing diverse shape-capping agents during the hydrothermal synthesis, the initial Ti-O bonds undergo dissociation, leading to a controlled

rearrangement of atoms and emergence of distinct exposed facets in the resulting single crystals^{25, 26}. By using different proportions of two shape capping agents, Cl⁻ and F⁻, specific single crystals like octahedral, cubic, and truncated structures can be achieved²⁷.

These single crystals in the anatase form contain three main facets with different surface energies: {001}, {101}, and {010} with surface energy of 0.9, 0.44, and 0.53 J/m², respectively²⁵. Since the coordination and orientation of the atoms in each facet are different, the activity and reactivity of the facets will also be varying^{28, 29}. Recent study by Zabara et al. showed that not only does the surface energy of the facets play a significant role in an electrochemical system, Fermi energy level and band gap of the each morphology can be altered²⁷. Therefore, one of the key role players in the Li⁺ storage kinetics and performance of nanostructured titania is the type of the exposed facets to the electrolyte.

It is widely believed that {001} planes of anatase thanks to presence of wider crystalline channels and lower energy barriers facilitate faster diffusion of Li⁺ and results in a superior Li⁺ rate performance³⁰⁻³². Cheng et al.³³ reported that the morphologies with higher amount of {001} facets show a lower insertion energy barrier compared to the {101} facets, and consequently, the low index facets shows a superior rate performance. Chen et. al.^{34, 35} showed an excellent columbic efficiency and rate performance for the two different morphologies of the anatase obtaining {001} facets. Although the importance of presence of {001} facets has been already emphasized in the literature, there is still a knowledge gap regarding the facet-dependent Li⁺ adsorption potential, charge and mass transfer kinetics.

In this study, three well-defined morphologies of anatase TiO₂—cubic, truncated, and octahedral—were synthesized using a two-step hydrothermal method with tailored shape-capping agents, resulting in single crystals with exposed {001}, {100}, and {101} facets. Electrochemical characterization revealed that cubic and truncated morphologies, enriched in high-energy {001} facets, exhibited significantly enhanced capacity retention, and more distinct lithiation behavior compared to octahedral particles with dominant {101} facets. Despite initial variations in coulombic efficiency, high-energy facets demonstrated superior long-term stability and interfacial performance. These results not only establish a clear, mechanistic link between facet identity and Li⁺ storage dynamics in anatase, but also demonstrate an experimental blueprint, precise facet control combined with multimodal electrochemical and structural interrogation, for isolating surface-driven transport and interface phenomena. Importantly, this approach is broadly transferable: it can be applied to emerging electrode materials or conventional solids that can be synthesized with tunable crystal faces, providing a general strategy to guide facet engineering, validate computational models, and accelerate the rational design of next-generation intercalation electrodes.

2. Experimental

2.1. Materials

TiO₂ powder (Sigma–Aldrich 325 mesh ≥99% trace metals basis). Carbon black (CB) (Vulcan XC-72R) was purchased from the fuel cell store. PVDF (*M*_w = 380,000 g/mol) powder was purchased from Solvay. N-Methyl-2-pyrrolidone (NMP) was purchased from Sigma-Aldrich. 1 M lithium hexafluorophosphate (LiPF₆) solution in ethylene carbonate (EC) and diethyl carbonate [EC/DEC = 50/50 (v/v)] was purchased from Sigma-Aldrich.

2.2. Preparation of TiO₂ nanoparticles

The preparation of the faceted TiO₂ nanoparticles was carried out hydrothermally in two step methods that was reported previously²⁷. Scheme S1 shows the synthesis procedure. Firstly, commercial TiO₂ powder is converted to sodium titanate in a hydrothermal vessel in a basic environment. 100 g of commercial TiO₂ anatase powder was poured and agitated into a 10M NaOH solution. The solution was transferred into a Teflon-lined stainless-steel autoclave. The autoclave was heated at 130°C for 48 h. After natural cooling, the obtained nanotubes acid washed using 0.1 M nitric acid solution until the pH is 5. After drying at 100°C, the achieved sodium titanate was used as the precursor for the single crystals' synthesis. Various capping agents in 100 mL were used for 200 mg of each morphology. A mixture solution of 2.0 M HCl and 0.03 M NaF was used for the cubic particles. A mixture solution of 2.0 M HCl and 0.045 M NaF was used for the truncated particles. A mixture solution of 2.0 M HCl and 0.045 M NaF was used for the truncated particles. 0.1 M LiClO₄ was used for octahedral particles. The already prepared titanate nanotubes were dispersed in separate solutions and transferred to the autoclave. The autoclave was heated for 12 h at 120, 160, and 200°C for cubic, truncated, and octahedral particles, respectively. The solutions were centrifuged, and the particles were washed with water to reach a neutral pH. After drying at 80°C for 2 h, the powders were calcined at 500°C for 2 h.

2.3. Physical and chemical characterization

The crystal structure of the formed nanoparticles was investigated using X-ray Diffraction (Bruker D2 Advance). The morphology of the formed TiO₂ nanoparticles were investigated using SEM (scanning electron microscope) and TEM (transition electron microscope). X-ray Photoelectron Spectroscopy (XPS) was used to study the surface of the TiO₂ nanoparticles and the formed interfaces.

Nitrogen adsorption/desorption isotherm (77 K) data were used to analyze the specific surface area and the porosity within the structure. The specific surface area was measured using adsorption/desorption values between *P/P*[°] of 0.05 and 0.35 with the

Brunauer–Emmett–Teller (BET) technique. The Barrett–Joyner–Halenda method was used to measure the pore size distribution (PSD) of the powders by the desorption branch of the isotherm. All samples were degassed for 24 h at 120 °C. A Zeiss LEO Supra 35VP SEM-FEG field-emission electron microscope at 3 kV operating voltage was used to investigate the surface morphology of the samples. A JEOL JEM 2000FX transmission electron microscope was utilized to analyze morphologies.

Gaussian peak fitting after background subtraction was performed for the acquired peaks using the LG4X interface in the Python programming language.

2.4. Electrochemical characterization

The electrode slurry including active material, CB, PVdF, and NMP was mixed overnight, stirring at 700 rpm. The slurry was bladed on a copper foil followed by drying initially at 80 °C for 4 h, and then put into 130 °C overnight. The electrodes were cut into 15 mm diameter circles with an average areal mass loading of 1.46 ± 0.3 mg/cm². CR 2025-coin cells were used to assemble the half cells under an argon-filled glove box [Jacomex GP (Campus)]. The utilized two-electrode system included Celgard PP, Li metal chips, and active material-based electrodes as the separator, the counter electrode, and the working electrode, respectively. The standard electrolyte including 1 M LiPF₆ in EC/DEC (1:1, v/v) was used within the half cells.

For the cyclic voltammograms (CV) test, a Princeton Applied Research PARSTAT MC system was used. CV tests were carried out within 1.0–3.0 V (vs Li/Li⁺) using a 0.1 mV/s scan rate. To perform the galvanostatic charge/discharge cycle tests, an MTI battery analyzer was utilized at various current densities (0.2C, 1C, 2C, and 4C) (1C=168 mA/g) within 1.0–3.0 V (vs Li/Li⁺). The electrochemical impedance test was performed within a frequency window of 10 mHz–1 MHz and an AC amplitude of 10 mV using the PARSTAT MC system. Multiple sweep rate CV tests (with the scan rates of 0.1, 0.5, 1, 5, and 10 mV/s) were done. The galvanostatic intermittent titration technique (GITT) was done by applying a constant current pulse of short duration (15 min), and resting for 3 h. After 100 cycle testing, the electrodes were dismantled and washed using DEC solution within the glove box. XPS, XRD, and SEM analysis were done on the electrodes.

3. Results and Discussions

3.1. Physical Characterization

SEM images show the various morphologies obtained from the synthesis. Fig. 1(a) and 1(b) show that the obtained cubes possess a bimodal structure in the same batch of synthesis. Based on the distribution histogram, Fig. 1(i), the average particle size (based on the length of the cubes) is 103 and 227 nm for Fig. (a) and Fig. (b), respectively. Fig. 1(e) and (f) show the TEM images of the cubes. As shown in Fig. 1(f), {001} facets are

comprised 33% of all the exposed facets. Fig. 1(c) shows the SEM image of truncated morphology. The average length of the base and edge of truncated particles is 344 and 247 nm, respectively. TEM image (Fig. 1(g)) shows two types of facets for this morphology. {001} facets are comprised around 70% of all facets. Therefore, truncated morphology has larger exposure of {001} compared to the cubes. Fig. 1(d) show the SEM image of octahedral morphology. The finest and most homogeneous distribution of the nanoparticles belongs to octahedral samples (Fig. 1(i)). The average length of edges for the octahedral particles is 65 nm. These measurements become more important for the calculation of volumetric density of each morphology in the diffusion coefficient estimation. TEM image (Fig. 1(h)) shows that this morphology has only one type of the exposed facet {101}.

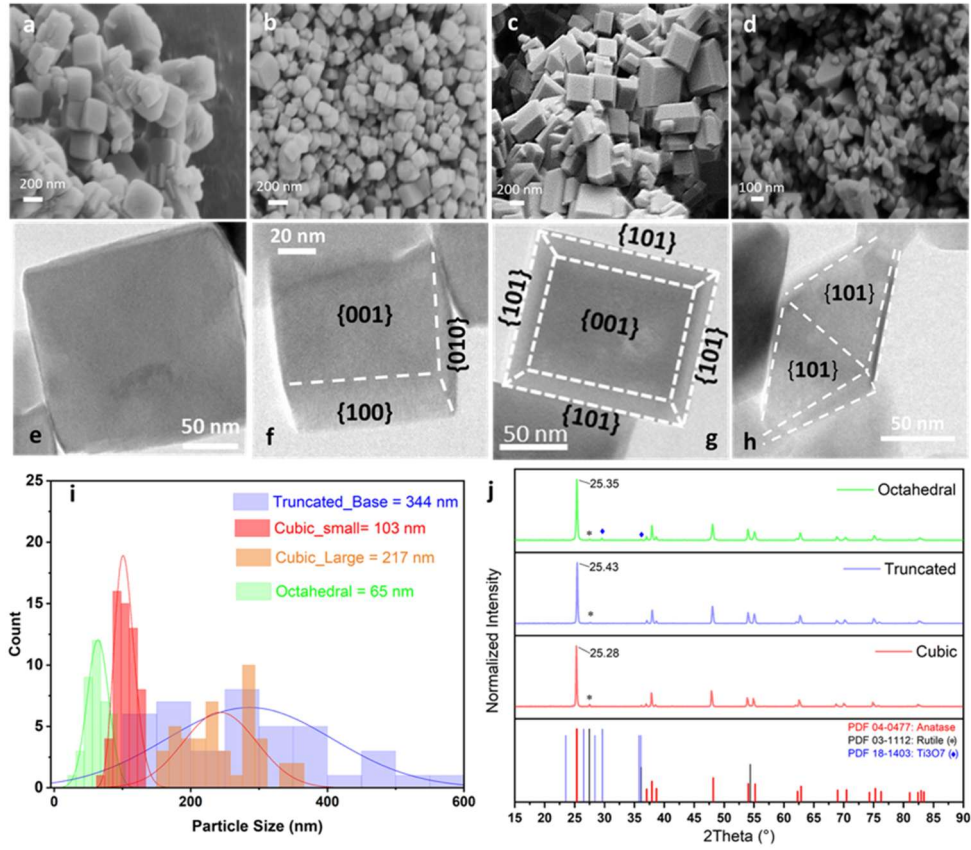


Fig. 1. SEM and TEM images of TiO₂ single crystals: (a, e) and (b, f) cubic in different size orders, (c, g) truncated, and (d, h) octahedral. (i) Particle size distributions plot of various morphologies based on SEM images. The number in legend shows the average value of particle size for each morphology. (j) XRD patterns of the samples.

Fig. 1(j) shows the XRD patterns of the single crystals with different morphologies. The major TiO_2 phase for all of the morphologies is anatase (PDF 04-0477) with (101), (103), (004), (112), (200), (105), (211), (213), (204), (116), (220), and (215) diffraction planes at 2θ values (of octahedral single crystal) of 25.3, 37.02, 37.90, 38.59, 48.03, 53.95, 55.07, 61.9, 62.73, 68.82, 70.28, and 75.11°, respectively. There is a slight shift of the intense peaks by changing the morphologies, for instance for the most intense peak (101), 2θ values are 25.35, 25.43, and 25.28°, for octahedral, truncated, and cubic morphologies, respectively. Based on Bragg's law, the interlayer spacing of (101) planes are 1.79, 1.79, and 1.80 Å for truncated, octahedral, and cubic, respectively. d-spacing from the bulk shows almost no difference, therefore, spacing of each facet needs to be calculated separately.

The dominating facets in the anatase, {100}, {101}, and {001}, has been studied in the literature^{19, 36, 37}. SEM and TEM images (Fig.1a-h) show the existence of these facets in the synthesized nanoparticles. Each facet could have an impact on Li-ion insertion properties due to the spacings on their pathways. It is assumed that larger interlayer spacings in the exposed facets result in easier Li-ion insertion. Therefore, based on the calculations in the literature^{36, 37}, the atomic structure of each facet is drawn and shown in Fig. S1.

According to Fig. S1, d_{020} and d_{200} show the similar average interlayer spacing of 1.892 Å. However, the interlayer spacing of {101}, $d_{202} = 1.17$ Å, is much lower compared to the others. When examining the Li-ion pathways, the {001} facets display a densely packed structure, Fig. S1(a), making it challenging for Li-ions to diffuse effectively. In contrast, the exposed facets of {010}, {101}, and {100} exhibit accessible voids with an average size of 0.96 Å. Kinetically, the larger interlayer spacing is expected to facilitate easier Li-ion diffusion within the structure. Additionally, the presence of voids in these exposed facets can further enhance the smooth intercalation of Li-ions. Therefore, facets with both adequate interlayer spacing and accessible openings, particularly the {010} and {101} facets, are likely to be more favorable for Li-ion intercalation. This structural arrangement allows for a balance between stability and ion mobility: the dense {001} facets contribute to overall stability (which will be discussed in the post-mortem section), while the more open {010} and {101} facets offer pathways that lower diffusion barriers for Li-ion transport. As a result, optimizing the exposure of these facets may improve the performance of anatase enhancing both rate capability and cyclability.

Based on these assumptions, it is expected that octahedral structure may obtain less stability because of lack of {001} facets but rather good diffusion behavior thanks to 100% contribution of {101} facets. The truncated sample obtaining around 70% of {001} facets are expected to have higher stability and moderate diffusion behavior (with a 30% of {101} facets). Finally, cubic samples by possessing equal contribution of {001}, {010}, and

{001}, and lack of {101} facets, are expected to show the superior kinetic behavior. It is worth to mention that since the surface energy of the {001} is highest compared to the other structures, initially, the higher chemical reaction with electrolyte could be also expected on the samples with {001} facets and may contribute to higher initial capacity losses. However, since the particle size of the samples are not similar in this study, the N₂ adsorption/desorption was carried out to normalize the areal contribution of each facet.

Fig. 2(a) shows the N₂ adsorption/desorption isotherms of all three morphologies. All samples showed type II adsorption isotherms with H3-type hysteresis loops. H3 hysteresis loop is found in solids with slit-shaped pores³⁸ consistent with the SEM images. The cohesion pressure for the octahedral isotherm is relatively higher compared to the two other samples, representing the larger existing porosities. Truncated and cubic samples show almost the same cohesion pressure. Table 1 shows that the pore volume for the octahedral nanoparticles is almost 10 times larger than others, which is mainly due to interparticle pores. BET surface areas for the octahedral, cubic, and truncated samples are 18.0, 5.4, and 5.6 m²/g, respectively (Table 1). These results are in line with the particle size distribution measurements and emphasize that the octahedral nanoparticles obtain a higher specific surface due to their particles size. To get an insight over the role of each facet in Li-ion insertion, calculated numbers will be utilized to obtain the areal capacity of each morphology based on the weight of the active material of electrodes.

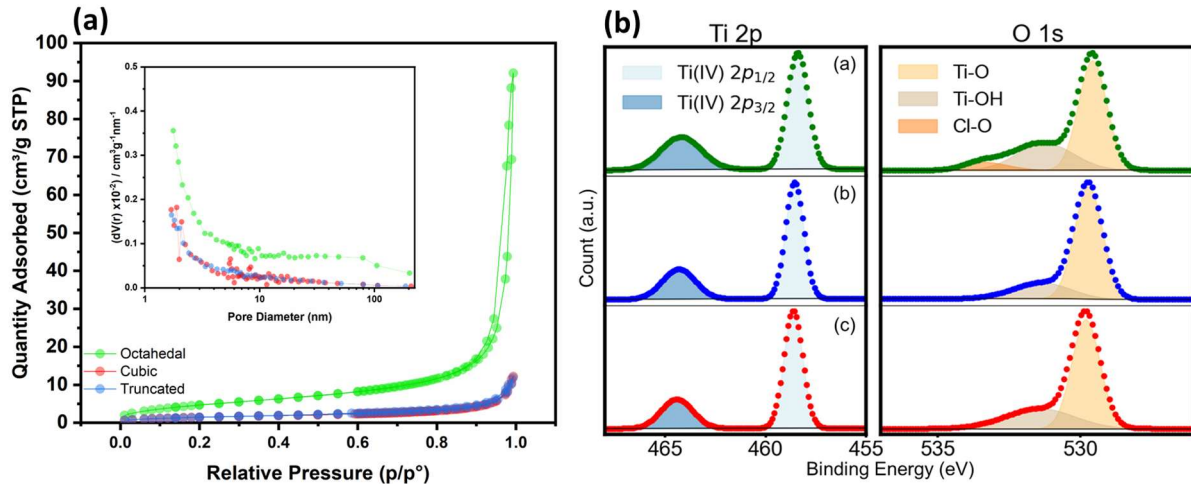


Fig. 2. (a) BET isotherms and BJH pore size distribution curves for all three morphologies. (b) XPS scans for the Ti 2p and the O 1s regions of the prepared TiO₂ nanoparticles with (i) Octahedron, (ii) Truncated, (iii) Cubic morphologies.

Table 1. The specific surface area, pore volume, and the average pore size of the nanoparticles obtained from the desorption branch of the isotherm.

Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)
Octahedral	18.0	0.143	10.7
Truncated	5.6	0.018	7.1
Cubic	5.4	0.019	6.7

Fig. 2(b) illustrates the XPS scans conducted on the prepared nanoparticles for the Ti 2p and O 1s regions. In the Ti 2p region, the obtained peaks for all morphologies exhibited a characteristic pattern consisting of two peaks, indicative of the 2p spin-orbit coupling of the Ti⁴⁺ oxidation state. These peaks were observed with a separation distance of 5.8 eV and an area ratio of 1:2.³⁹⁻⁴¹ Analysis of the oxygen 1s region revealed the predominant presence of lattice Ti-O bonding alongside surface Ti-OH. The peak ratio for each morphology was calculated, with the truncated morphology displaying the highest ratio at 3.5, followed by the octahedron at 2.2 and the cubic at 2.0. Notably, the octahedron particles exhibited an additional peak in the O 1s region at 533.5 eV, attributed to the Cl-O bonding originating from the shape-capping agent employed during the preparation step (LiClO₄). Using the calculated Fermi level of the particles by fitting the XPS curve at the zero point, the highest Fermi level belongs to truncated structure (2.3 eV above the valence band) followed by 2.1 eV and 1.8 eV for cubic and octahedral sample, respectively²⁷. Fermi levels coupled with the measured surface charge of the nanoparticles are in line with the presence of high energy facets, {001}, in the truncated and cubic, and low energy facets, {101}, in the octahedral nanoparticles²⁷, since these surfaces have higher amount of undercoordinated Ti atoms leading to oxygen vacancies. Therefore, it could be expected to see higher chemical activity of the truncated and cubic nanoparticles at least in initial cycles.

3.2. Electrochemical characterization

The modification of TiO₂ morphology is proposed to influence electrochemical lithium storage by altering the TiO₂/electrolyte interface and affecting the kinetics of Li⁺ insertion at specific facets. To investigate these effects, we employed potential scans, galvanostatic cycling, and electrochemical impedance spectroscopy. Current values were normalized to the surface area of TiO₂ particles on each electrode, as determined through BET surface area analysis, ensuring accurate comparison across samples.

3.2.1. Li⁺ insertion potential

CV results of each morphology demonstrated variation in both insertion/de-insertion potentials as well as the current values, indicating the high impact of the facet-dependence of the Li⁺ insertion process. Fig. 3 shows the CV data of the different

morphologies scanned between 1.00 and 3.00 V vs. Li^+/Li at 0.10 mV/s. In Fig. 3(a) which is for octahedral morphology's 1st cycle, dominated by {101} facets, two peaks at around 1.68 and 2.23 V at cathodic and anodic sweeps appeared respectively. These peaks can be attributed to the tetragonal to orthorhombic transition while Li^+ insertion (Ti^{+4} reduction) and extraction (Ti^{+3} oxidation)⁴². Other than a slight drop in the cathodic current peak after the 1st cycle due to the lattice rearrangement and parasitic reactions, there is no remarkable change in the structure till the 5th cycle.

The truncated and cubic TiO_2 , however, showed different behavior (Fig. 3(b) & (c)). For the truncated morphology (Fig. 3(b)), the cathodic sweep shows two peaks at different potentials (1.48 and 1.65 V) in the 1st cycle. This difference can be explained by the presence of the two insertion facets in the truncated morphology, the peak at 1.65 V is similar to the one already seen in octahedral structure, which can be attributed to {101} facets, and peak at 1.48 V can be attributed to the lithiation of {001} facet surfaces.

For the cubic samples (Fig. 3(c)), an initial reduction peak appears at 1.44 V, suggesting hindered Li^+ intercalation, likely through the dense {001} plane. In the second cycle, a new peak emerges at 1.66 V, indicating lattice reconstruction that facilitates Li^+ intercalation along a different crystallographic direction. Rather than facet-specific reactions, these potentials may reflect intercalation through specific planes or directions—initially along the {001} plane (high energy surface and irreversible lithiation), followed by more thermodynamically favorable insertion pathways such as the [100] and [010] directions (between the (001) planes) after structural rearrangement.

By measuring the redox peak separation in the 1st cycles, higher overpotential is needed for the truncated (0.83 V) and cubic (0.89 V) than octahedral samples (0.66 V), which means a higher thermodynamic barrier for the lithiation and extraction of ions. However, after the 5th cycle, the overpotentials reduced to 0.51, 0.52 and 0.45 V for truncated, cubic and octahedral particles respectively. This suggests that after surface restructuring the de/intercalation occurs on similar sites.

As shown in Fig. 3 (b and c), after five cycles in both cubic and truncated morphologies, the characteristic cathodic anatase peak for Li^+ insertion appears at 1.66 V, with no additional peaks observed at higher potentials during previous cycles. The intactness of the structure after 1st and 100th cycles (post-mortem analysis section) suggests that there is no strong transformation in the lattice structure. Therefore, the influence of facet variation has a great effect on the lithiation during the initial cycles, after which the bulk diffusion becomes dominant. However, these facets will have a crucial role on the side reactions occurring on the surface. Moreover, in all morphologies, the anodic peaks exhibit a transition from a mass transport-limited regime to a surface reaction-dominated

regime, as evidenced by the emergence of more Gaussian-like peak shapes⁴³ conforming the surface reconstruction.

The tendency of the Li^+ to initially be adsorbed onto the closely packed facets rather than the other pathways can be attributed to the higher surface energy and Fermi level of the {001} facets. As a result, for the initial cycle in CV, we are reaching higher current values for cubic ($\sim 20 \text{ mA/cm}^2$) followed by truncated ($\sim 15 \text{ mA/cm}^2$) and octahedral ($\sim 10 \text{ mA/cm}^2$). However, this surface reaction, although parasitic in nature, stabilizes {001} facets and creates a passivating layer preventing further interaction with the electrolyte.

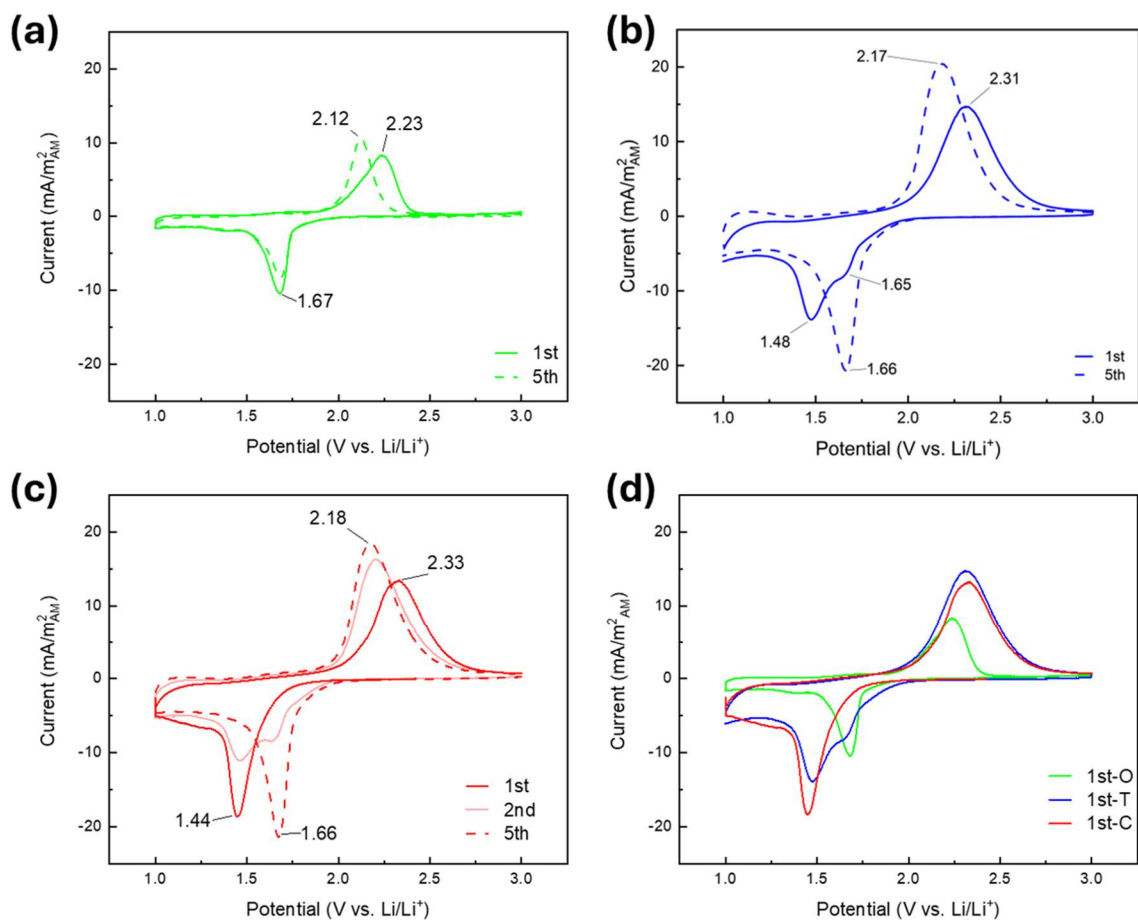


Fig 3. 1st and 5th cycles of the CV of (a) octahedral, (b) truncated, and (c) cubic samples. (d) Overall CV of the 1st cycle for all morphologies.

3.2.2. Galvanostatic Cycling Performance

Fig. 4 illustrates the cycling performance of the samples at 0.2C over 100 cycles. It should be noted that the capacities are given per unit area, not per mass. The aim is to have a better comparison, since this study aims to clarify the interface interactions. As can be observed in Fig. 4(a), the cubic morphology exhibits the highest areal capacity (216 mAh/g), followed by the truncated morphology (124 mAh/g), while the octahedral morphology displays the lowest capacity (276 mAh/g). Clarification is required to account for the differences in the ranking of specific capacities (not areal ones). Octahedral particles expose all crystallographic facets for intercalation; by contrast, cubic and truncated particles expose only approximately two-thirds and 30% of their facets, respectively.

However, because surface interactions play a crucial role, the overall performance is determined not just by the number of accessible facets, but by the nature of the specific surfaces exposed. Viewed on an areal capacity basis, what governs intercalation is the accessibility of entry points. Cubic particles therefore offer more open surface sites and greater accessibility than the other morphologies considered.

After 100 cycles, cubic particles retain the highest areal capacity, whereas octahedral particles exhibit the lowest (48% capacity loss). This is attributed to higher stability of the cube facets to side reactions than the other morphologies. Therefore, the superior areal capacity of cubic morphology likely arises from the stability of its exposed crystallographic facets and the facile intercalation of Li^+ .

Coulombic cycle inefficiency (CCIE), defined as the cycle-by-cycle cumulative loss complementary to coulombic efficiency. In Fig. 4(b), CCIE results show that octahedral samples initially have high coulombic efficiencies, but after initial cycles there is a steep increase in the CCIE of the samples resulting in a worse overall performance. In contrast, truncated particles exhibit an initially high inefficiency; their CCIE increases with cycling, but the rate of increase is lower than that observed for octahedral particles. The initial inefficiency of the cubic particles is slightly greater than that of the octahedral particles, but the cubes exhibit the lowest subsequent rate of increase. Ultimately, the cubic particles attain the flattest CCIE profile, indicating the greatest stability among the three morphologies.

The superior stability of certain morphologies against side reactions can be rationalized at several structural levels. In particular, comparisons between morphologies should account for the relative areas of exposed crystallographic facets, since the facet distribution differs between shapes (Physical Characterization section). By multiplying the fractional facet exposure for each morphology by its measured specific surface area, one obtains the facet-specific surface area that determines the relative number of reaction

entry sites (Figure S2). Examination of the CCIE curve together with the relative facet surface areas in Figure S2 suggests that the high fraction of {001} facets underlies the elevated initial inefficiency. This explains why truncated particles show the worst initial performance; by contrast, octahedral particles—with no {001} facets—do not display measurable initial parasitic reactions. This phenomenon appears only during the initial cycles. Subsequently, since the {001} sites are all occupied, the rate of side reactions increases for particles dominated by {101} facets; as the octahedral particles possess the highest {101} fraction, they record the greatest CCIE.

Coulombic inefficiency provides an indirect but quantitative proxy for parasitic side reactions that consume charge; low coulombic efficiencies therefore reflect enhanced side-reaction activity⁴⁴. The CCIE profiles may be interpreted as reaction-progress (decomposition) curves: the ordinate reports the accumulation of side-reaction product per cycle, while the abscissa is cycle number rather than continuous time. Heterogeneous degradation on TiO₂ surfaces is commonly described by pseudo-first-order kinetics under conditions where the reactive species or surface sites are in quasi-steady state⁴⁵. Fitting the CCIE profiles with first-order kinetics shows that the octahedral and truncated morphologies are well represented by a single first-order rate constant, whereas the cubic morphology exhibits two distinct kinetic regimes - a rapid initial phase during approximately the first ten cycles followed by a slower secondary phase (Table S1). This two-regime behaviour is consistent with either two parallel parasitic pathways or a change in the rate-limiting step and is therefore well captured by a piecewise pseudo-first-order model that assigns separate rate constants to the early and late regimes⁴⁶.

Examination of Table S1 indicates that the cubic particles undergo rapid degradation during the initial ~10 cycles, with an apparent rate constant $k_{\text{cube,init.}} = 1.63 \times 10^{-2}$ 1/cycles. This fast early loss is likely associated with the {100} facets; after ~10 cycles, the cubes stabilize and the rate falls to 0.26×10^{-2} 1/cycles. By contrast, octahedral particles display a persistently high degradation rate attributed to {101} facets (1.64×10^{-2} 1/cycles). Truncated particles exhibit intermediate behavior, with a degradation rate of 0.85×10^{-2} 1/cycles. Although the larger surface area of the octahedral morphology contributes to an increased absolute extent of side reactions, normalization of the rates to specific surface area shows that low-energy {101} facets nevertheless sustain comparatively higher parasitic activity per unit area.

Figure 4(c) presents the voltage profiles recorded at 0.2 C for the first and hundredth cycles. The octahedral morphology exhibits a pronounced, peak-like overpotential during charging that is not observed for the cubic or truncated samples. This feature has previously been reported for anatase and rutile TiO₂^{47, 48}. and analogous profiles in other materials have been attributed to multiphase coherency strains that develop during delithiation⁴⁹. A more detailed discussion of the mass-transport implications of this

behavior is given in the Mass Transfer section. The cubic morphology displays a distinctly sloping voltage profile that contrasts with the flatter profiles of the other morphologies. Pronounced voltage slopes are characteristic of pseudocapacitive behaviour, which can arise from surface redox pseudocapacitance or intercalation pseudocapacitance.⁵⁰ Although TiO_2 is not generally regarded as a pseudocapacitive material, the sloping response associated with the $\{100\}$ facets suggests faster ion insertion at those surfaces, analogous to intercalation-type pseudocapacitance. For this reason, cubes show a very wide but smooth lithiation slope, and there is almost no sharp reduction in potential through the lithiation process, which is in line with the observed reconstruction behavior in its CV. Similar voltage profile was reported in hydrothermally synthesized nanotubes⁸ suggesting a similar insertion mechanism. Through further cycling, the octahedron and truncated sample bear great resemblance to the normal anatase structure which consists of a long plateau followed by a sharp drop in the potential in the final stages of the lithiation.

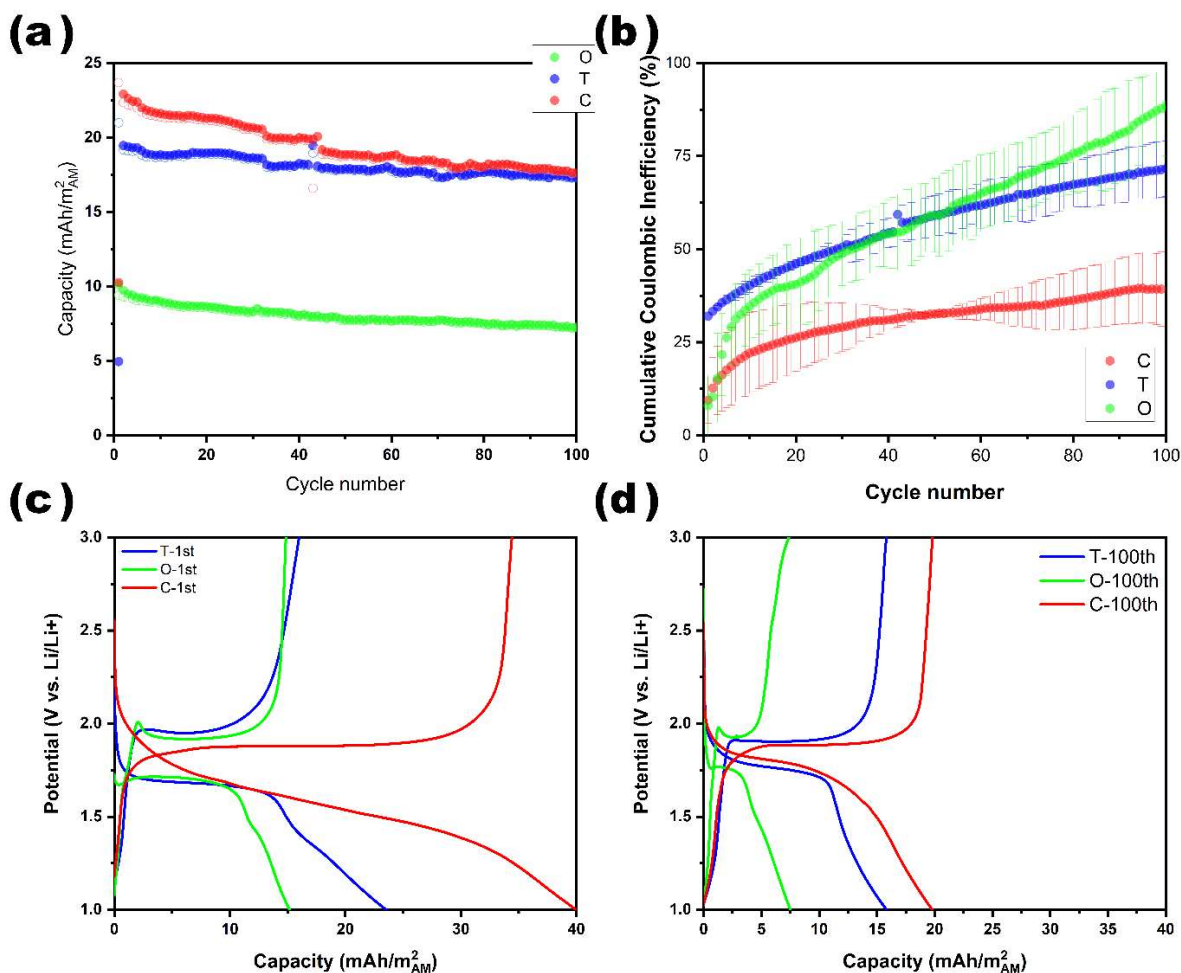


Fig. 4. (a) Cycling performance of the various morphologies, filled and vacant circles show the discharge and charge capacity, respectively. (b) 1st and (c) 100th cycle voltage profile. (d) Cumulative coulombic inefficiency through cycling.

Fig. 5 shows the rate performance of the samples at 0.2C, 1C, 2C, 4C and 8C. The normalized capacities indicate that, at all tested current densities, the cubic morphology outperforms the truncated and octahedral morphologies, respectively. As discussed above, this superior rate performance is attributable to the {100} facets, which facilitate more rapid lithiation. The voltage profiles recorded during the rate-performance tests (Fig. 5(b–d)) closely resemble those observed during standard cycling, displaying no appreciable divergence between the two protocols.

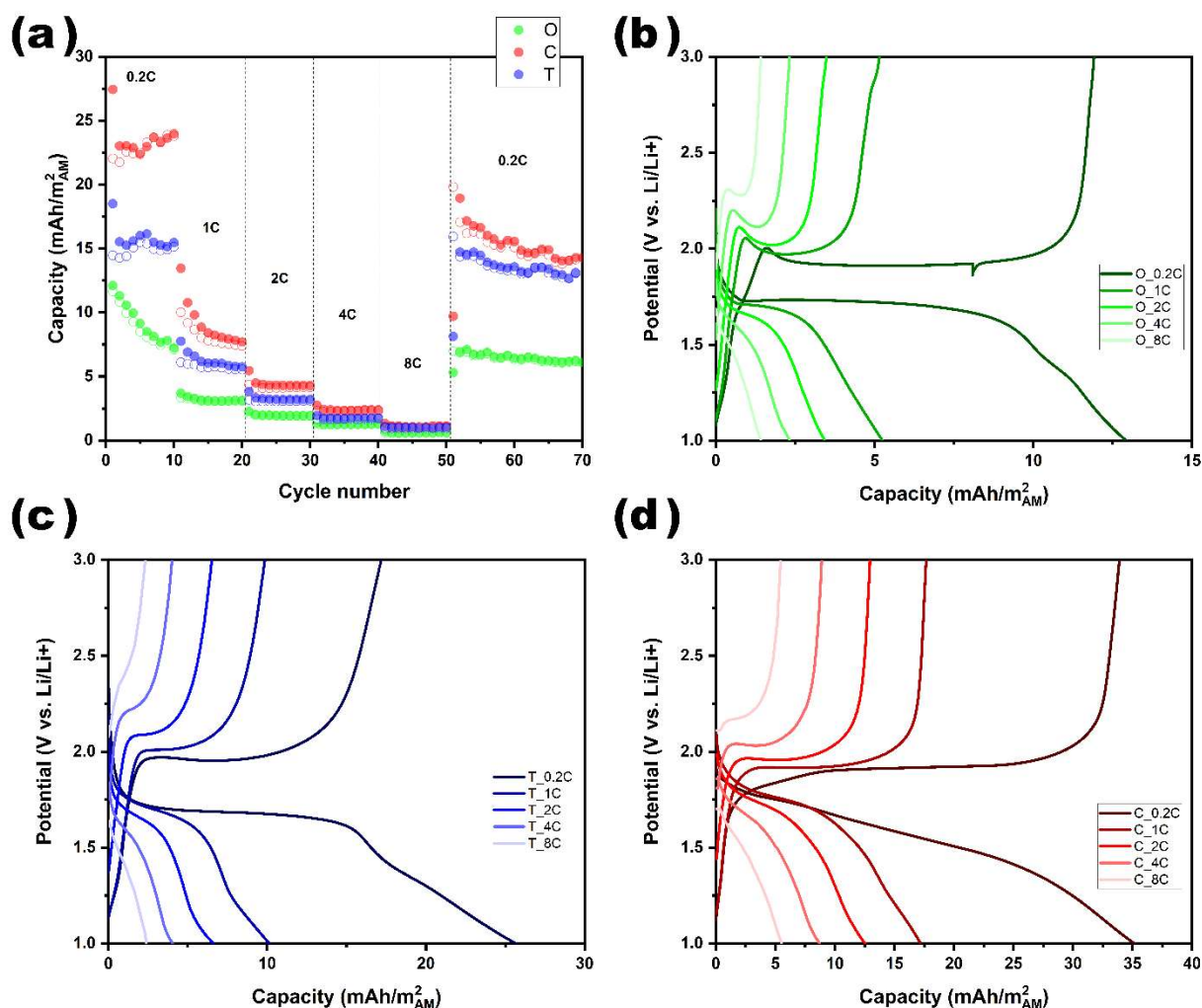


Fig. 5. (a) Rate performance of the various morphologies, filled and vacant circles show the discharge and charge capacity, respectively. (b)-(c) show the voltage profile of each morphology in different current densities.

3.2.3. Capacitance and Mass Transfer

The current observed in the CVs can be attributed to two main factors: the faradaic contribution from the diffusion-limited Li-ion insertion process along with pseudocapacitance, and the nonfaradaic contribution arising from the double-layer charging effect. The TiO₂ nanoparticles are anticipated to exhibit significant capacitive behavior due to their high surface area. The extent of this capacitive contribution is expected to vary based on morphology, which is determined by the formed facets. By analyzing the CVs at different sweep rates, it is possible to distinguish between the current resulting from the diffusion-limited Li-ion insertion process and the capacitive current. To achieve this, the relationship of the peak current is explored using the following equation:

$$I = av^b \quad (1)$$

Where I is the current, v is the sweep rate, and a and b are the changing variables calculated by plotting the $\log I$ vs. $\log v$. It is widely recognized that the Faradaic diffusion-controlled process exhibits a slope of 0.5, whereas capacitive behavior is characterized by a slope of 1.0.⁵¹

The CVs obtained at various sweep rates, ranging from 0.1 to 10 mV/s, are illustrated in Fig. 6(a-c) for the three different morphologies. Initially, the peak currents for both oxidation and reduction scans were identified. A pair of peaks can be detected for all morphologies. b values were calculated using Fig. 6(d). b values which are ranging from 0.40-0.54 show a diffusion-controlled behavior for all morphologies; therefore, there is not significant capacitive behavior contribution in both Li⁺ extraction (anodic peaks) and Li⁺ insertion (cathodic peaks).

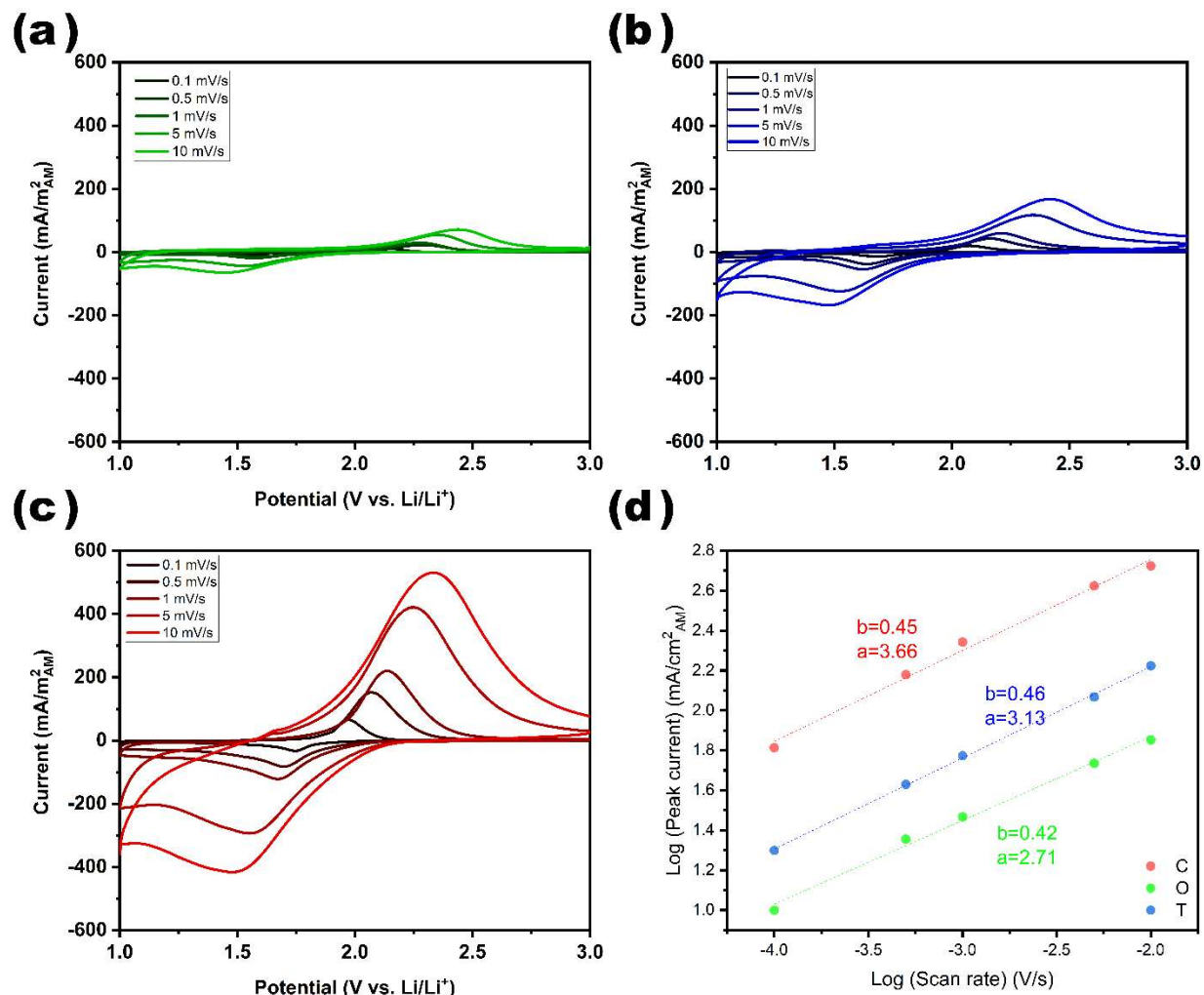


Fig. 6. CV with multiple sweep rates of (a) octahedral, (b) truncated, and (c) cubic samples. (d) Log (peak current) vs. Log (scan rate).

Further details on the diffusion process were studied by GITT tests. The diffusion kinetics of the ions in an electrode can be estimated by comparing its chemical diffusion coefficient (D). D values can be estimated by galvanostatic intermittent titration technique (GITT). Following Fick's second law with a semi-finite diffusion boundary condition and considering the equality rate of transferring of electrons through outer circuit with the charge flow through the electrolyte till the surface of electrode, the researchers have suggested the following equation⁵²:

$$D_{Li^+} = \frac{4}{\pi \cdot \tau} \left[\frac{m_B \cdot V_m}{M_B \cdot A} \right]^2 \left[\frac{\Delta E_s}{\Delta E_\tau} \right]^2$$

where m_B and M_B represent the active mass per electrode and the molar mass of TiO_2 , respectively. For estimating the molar volume, V_m , the theoretical volume and area of

each morphology was calculated based on the average particle size. Using the BET surface area, the mass of each particle for each morphology (in average size) was estimated. By dividing the volume of each particle by the mole (calculated from mass), V_m was estimated. A was considered to be the surface area of the electrode. Therefore, the comparison of the chemical diffusion coefficient was done in a qualitative way. ΔE_s , and ΔE_r are the potential differences between the equilibrium potential and the excited potential after relaxation, and potential differences between the excited potential and the equilibrium potential before relaxation, respectively.

Fig. S3 shows the diffusion coefficient (D) and potential steps at different discharge states for the fresh cells and cells after 100 cycles of cycling. Table S2 summarizes the calculated initial D values for different morphologies. During the first cycle, cubic particles exhibit more than tenfold higher Li^+ diffusion coefficient than octahedral particles. Because the intercalation planes on the $\{101\}$ facets are not oriented perpendicular to the particle surface, Li^+ insertion is physically hindered along certain directions, which reduces the effective diffusion coefficient (Figure S1 & S4). Although both truncated and octahedral particles are dominated by $\{101\}$ facets, they exhibit different effective diffusion coefficients. This discrepancy can be attributed to particle size: the smaller octahedral particles are more susceptible to surface clogging by deposited side products, so a given amount of deposition produces a larger relative reduction in accessible intercalation pathways and thus a greater decline in effective diffusivity. After 100 cycles, the cubic morphology continues to display the largest diffusion coefficient during the initial stages of lithiation. This enhanced ion mobility correlates with the cycling data (Fig. 4a), which demonstrates that the cubic structure remains stable over the course of cycling. Although all morphologies show some decline in diffusivity with cycling, the decrease is particularly pronounced for the octahedral and truncated particles—most likely owing to more clogging of intercalation channels. This point is examined in the Post-Mortem section.

3.2.4. Electrochemical Impedance

Interpreting the EIS data for metal oxides becomes challenging, primarily due to the high inhomogeneous electrochemical surface area and the presence of a substantial Helmholtz capacitance at the interface with low impedance values at charge transfer reactions⁵³. Therefore, being acquainted with the impedance response of each component within the cell will help to simplify the EIS interpretation⁵⁴.

Utilizing Li metal as the counter and reference electrode in half cell system is expected to result in impedance contribution in high frequency regions caused by the SEI of Li metal. This will result in contribution from both Li metal interface and TiO_2 interface in the high frequency region^{54, 55}. The Nyquist plot in Fig. 7 (a & b) depicts the impedance response

of TiO_2/Li for all morphologies at their lithiated state (1 V vs. Li/Li^+) at their 1st and 100th cycle. The spectrum reveals three distinct regions: a high-frequency semicircle (100 kHz-5 Hz), a middle-frequency semicircle (5 Hz-100 mHz), and a low-frequency response (100 mHz-10 mHz).

Using the Equivalent circuit model in Fig. 7(c), the EIS data of TiO_2/Li cells were modeled. The first component is R_s showing the solution resistance. The high-frequency semicircle is modeled with a parallel combination of $R_{\text{intr.}}/\text{CPE}$ corresponding to the interfacial impedance of the Li electrode. Mid-range semicircle was related to the charge transfer reaction of TiO_2 impedance fitted with another R_{CT}/CPE . The low-frequency semicircle showed high capacitive impedance which is assumed to be related to the capacitive response of the high surface area TiO_2 nanoparticle electrode. This region was fitted with transmission line model which is suitable for such inhomogeneous and porous electrodes.^{56, 57} The model is composed of large number of interfacial R_k/CPE circuits modeling the TiO_2 charge transfer resistance and an internal resistances R_m representing the pore resistance. In the model the charge transfer resistance R_k is set to very high charge transfer resistance of $1\text{M}\Omega$ due to blocking boundary condition and the pore size to unity.

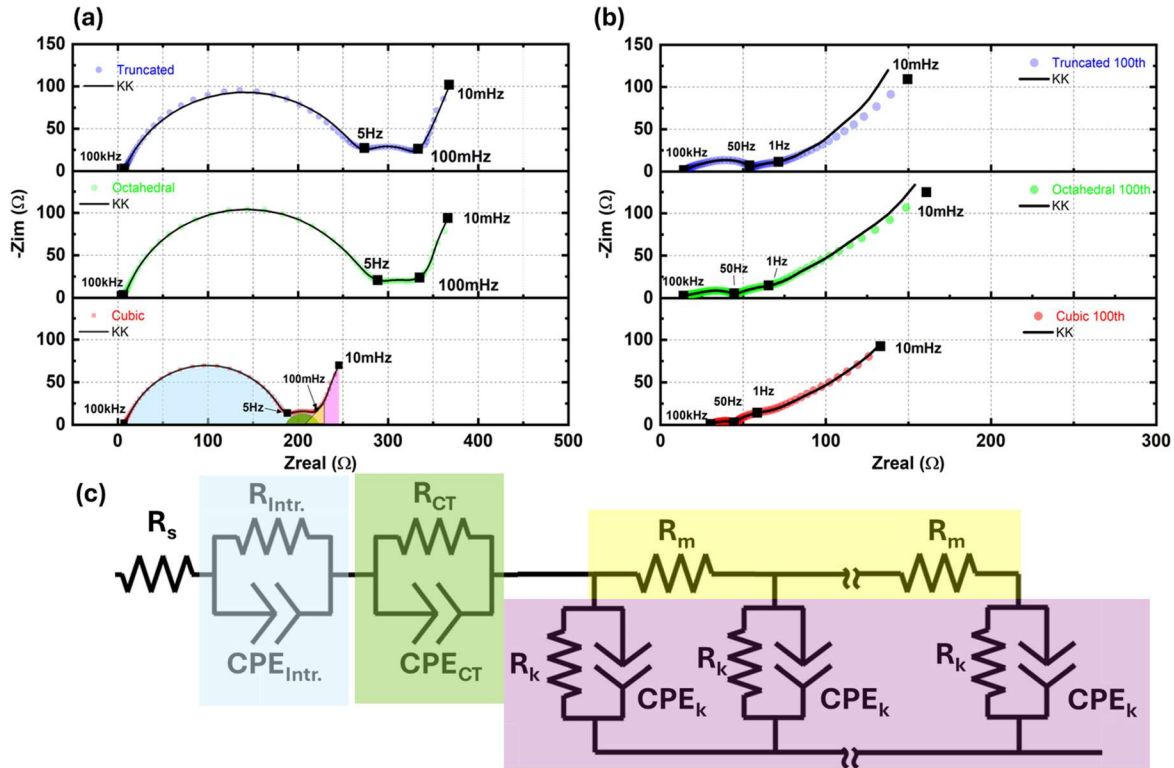


Fig 7. Nyquist plots of cells in their lithiated state for (a) the 1st cycle and (b) the 100th cycle. (c) Equivalent circuit used to fit the EIS data.

As can be observed from Fig 7(a & b) there is a large change in the impedance response between the 1st and the 100th cycle. Table S2 shows the fitted values based on the equivalent circuit for the 1st and 100th cycles of all morphologies at their lithiated states. During the initial cycle, the apparent interfacial resistance attributable to the Li metal is lowest for the cubic morphology and higher, and comparable, for the truncated and octahedral morphologies. Fresh Li typically undergoes electrolyte decomposition to form an SEI⁵⁸; however, as discussed in the CCIE section, the cubic cathodes undergo a rapid early parasitic decomposition. We propose that this cathode-side decomposition consumes electrolyte/reactive intermediates that would otherwise contribute to Li-side SEI growth, thereby attenuating SEI accumulation on the lithium and reducing the Li-side interfacial impedance. The fitted TiO₂ charge-transfer resistance in the mid-frequency region is lowest for the cubic sample ($22.3 \pm 5.9 \Omega$), reflecting its more open microstructure, intermediate for the octahedral sample ($32.6 \pm 12.1 \Omega$), and highest for the truncated sample ($49.8 \pm 8.5 \Omega$); this ordering parallels the first-cycle CCIE results. In the lowest-frequency region, pore resistance is lowest for the cubic then truncated samples and highest for the octahedral sample; the elevated resistance of the octahedra is consistent with deposition of side-reaction products that occlude pore space rather than with the formation of a stabilizing interfacial layer.

Following 100 cycles the impedance profile exhibits a pronounced reduction in the Li-metal interfacial resistance. Two non-exclusive mechanisms can account for this observation. First, the SEI can “mature” with cycling: structural reorganization and a shift toward more ionically percolating pathways reduce the effective resistivity of the interphase⁵⁹. Second, cathode-derived chemistry can change the SEI composition on the Li: decomposition of salt anions on transition-metal oxide surfaces can release fluoride that migrates to the negative electrode and deposits as LiF, a phase that has been reported to alter SEI transport properties and in some cases lower anode impedance⁶⁰.

After prolonged cycling, the charge-transfer resistance values converge for all morphologies, implying that the bulk of the crystalline lattice remains intact and does not experience pronounced deformation. This observation suggests that the differences in electrochemical behaviour are dominated by surface- and facet-level processes rather than by large-scale structural damage to the TiO₂ crystals.

The most informative spectral changes occur at low frequency, where R_M rises with cycle number—evidence of increasingly hindered Li⁺ transport and structural deterioration of the electrode pore network. This effect is particularly severe for octahedral particles, which generate more parasitic products that deposit on {101} surfaces; the resulting thicker, porous LiF layer increases tortuosity and blocks intercalation pathways, thereby elevating pore resistance (Post-mortem section). Cubic particles, in contrast, maintain

relatively low pore resistance, consistent with their reduced deposition and more open microstructure.

3.3. Post-mortem Analysis

It is well-known that apparent native SEI layer can be formed on top of TiO_2 particles spontaneously after contacting with EC-DEC electrolyte, and thanks to high lithiation potential, there is almost no electrochemically traditional SEI formation for TiO_2 -based electrodes⁶¹. Presence of humidity and extra functional groups could result in decomposition of the electrolyte and formation of SEI composed of inorganic compounds like LiF and Li_2CO_3 ⁶²⁻⁶⁴. To understand the reactivity of each facet with electrolyte in various conditions, the post-mortem analysis was done on the electrodes made of all morphologies. Accordingly, the cells were dismantled after resting in contact with the electrolyte for 24h, 5th cycle lithiation, and 100th cycle lithiation.

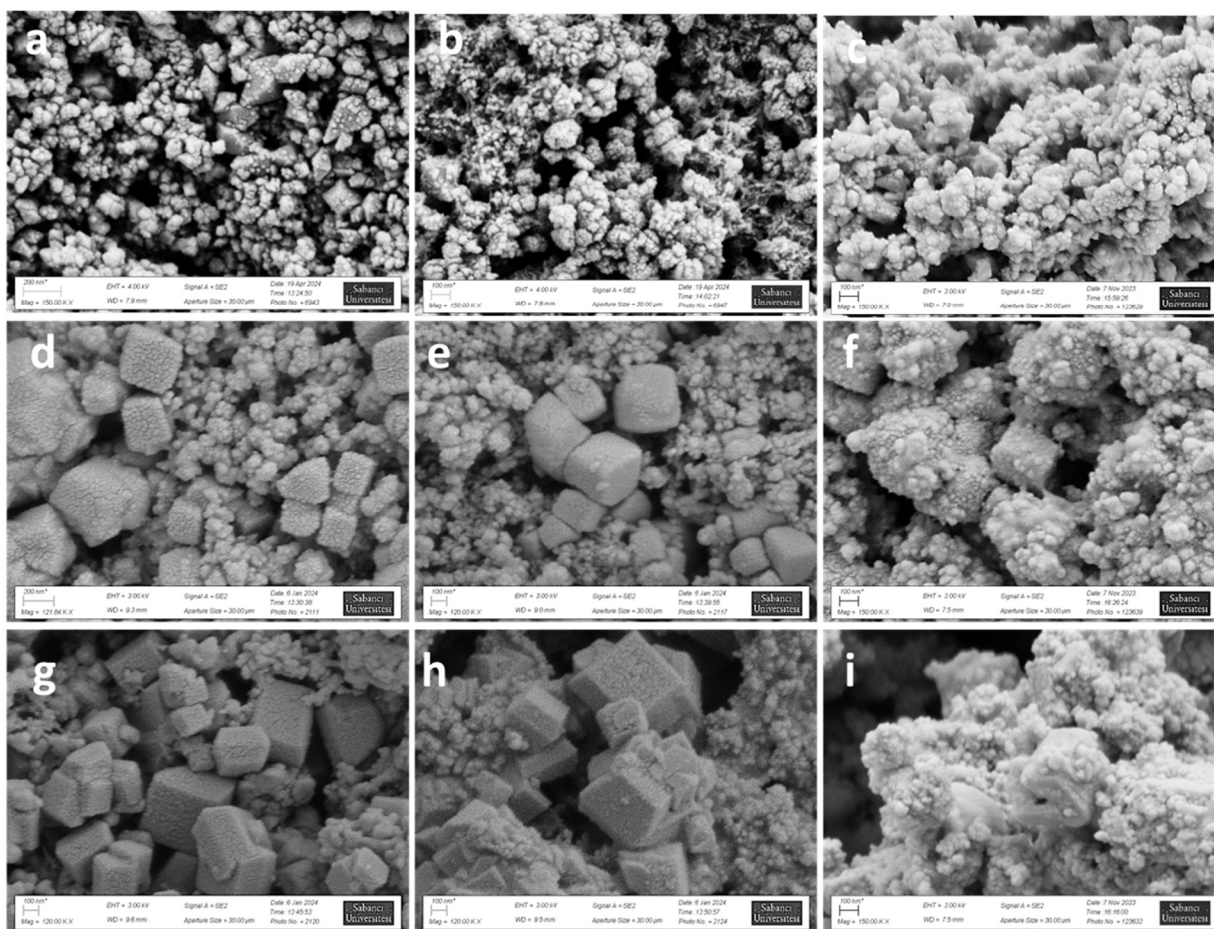


Fig. 8. SEM images of post-mortem octahedral electrodes at (a) 24 h rested after assembly, (b) after 5th cycle, and (c) after 100th cycle. (d)-(f) show similar images for the cubic electrodes. (g-i) show similar images for the truncated electrodes.

Figure 8 presents SEM images of post-mortem electrodes for each morphology. After 24-hour exposure to the electrolyte prior to cycling, the particles exhibited morphology-dependent surface responses. Octahedral particles show only mild surface deposition, whereas cubic and truncated particles are coated with a conformal, porous surface layer while their overall particle shapes remain discernible. The principal distinction between the truncated and cubic samples is that the truncated particles bear a noticeably denser surface coating. After five cycles, the cubic and truncated particles remain visually similar to their pre-cycling condition, exhibiting conformal surface coatings while retaining their original shape; by contrast, octahedral particles become covered by a less-conformal deposit that increasingly obscures their native morphology. Following 100 cycles the electrode surfaces are extensively coated for every morphology. The coating on octahedral particles is sufficiently thick and non-conformal that the original particle shape can no longer be identified. By contrast, cubic and truncated particles remain morphologically recognizable beneath a thick deposit, implying that their crystalline bulk remains intact while the surface is altered. In several truncated particles the deposit is concentrated on {101} facets, supporting the hypothesis of facet-selective parasitic deposition and its role in transport blockage.

The formed interface on the surface of the TiO₂ nanostructures after 100th cycle was characterized using XPS. Fig 9. shows the data for Li 1s, O 1s, C 1s, and F 1s regions. The XPS post-mortem spectra of the three morphologies show a Li 1s peak centered near 56.3 eV, which is consistent with LiF⁶⁵. This spectroscopic signature therefore identifies LiF as the principal inorganic precipitate formed by the parasitic reactions.

Deconvolution of the C 1s region reveals peaks assignable to carbon black (C–C, 284.8 eV), carbon singly bound to oxygen (C–O, ~286.5 eV), carbonyl/carboxyl species (C=O, ~288.4 eV), and PVDF-derived features (~289.9 eV)⁶⁶. Because the carbon-black signal remains prominent, the deposited surface layer after 100 cycles is not sufficiently thick to completely attenuate the substrate signal within the XPS probing depth.

The O 1s spectra for all electrodes deconvolve into three principal components: lattice oxygen of TiO₂ (~529.8 eV), surface carbonyl oxygen (C=O, ~531.5 eV), and oxygen singly bound to carbon (C–O, ~532.9 eV)^{66, 67}. The C–O and C=O features are consistent with organic carbonate species such as lithium alkyl carbonates observed on lithiated transition-metal-oxide electrodes. Such a lineshape in the O 1s region is typical for Li-transition-metal-oxide electrodes in Li-ion systems. Crucially, we do not observe a component at ~535 eV attributable to Li_xPF_yO_z (salt-derived phosphate/fluorophosphate

species bound via oxygen). The absence of this peak provides important evidence that decomposition of the PF_6^- salt does not contribute substantially to the oxygen-bound surface chemistry in these samples, and thus narrows the plausible surface-reaction pathways.

The F 1s spectra of all electrodes are dominated by a major component at ~ 684.9 eV, consistent with LiF formation. A higher-binding-energy component centered near ~ 687.2 eV is attributable to fluorocarbon species (likely residual PVDF binder). A minor feature at ~ 686.3 eV is consistent with substitutional fluorine in TiO_2 and the formation of surface TiF_2 ⁶⁸. Overall, the F 1s region is dominated by LiF, but the LiF signal intensity depends on particle morphology: octahedral electrodes exhibit the strongest LiF signal (in agreement with the electrochemical and post-mortem structural data), whereas cubic electrodes show substantially lower LiF content at the surface.

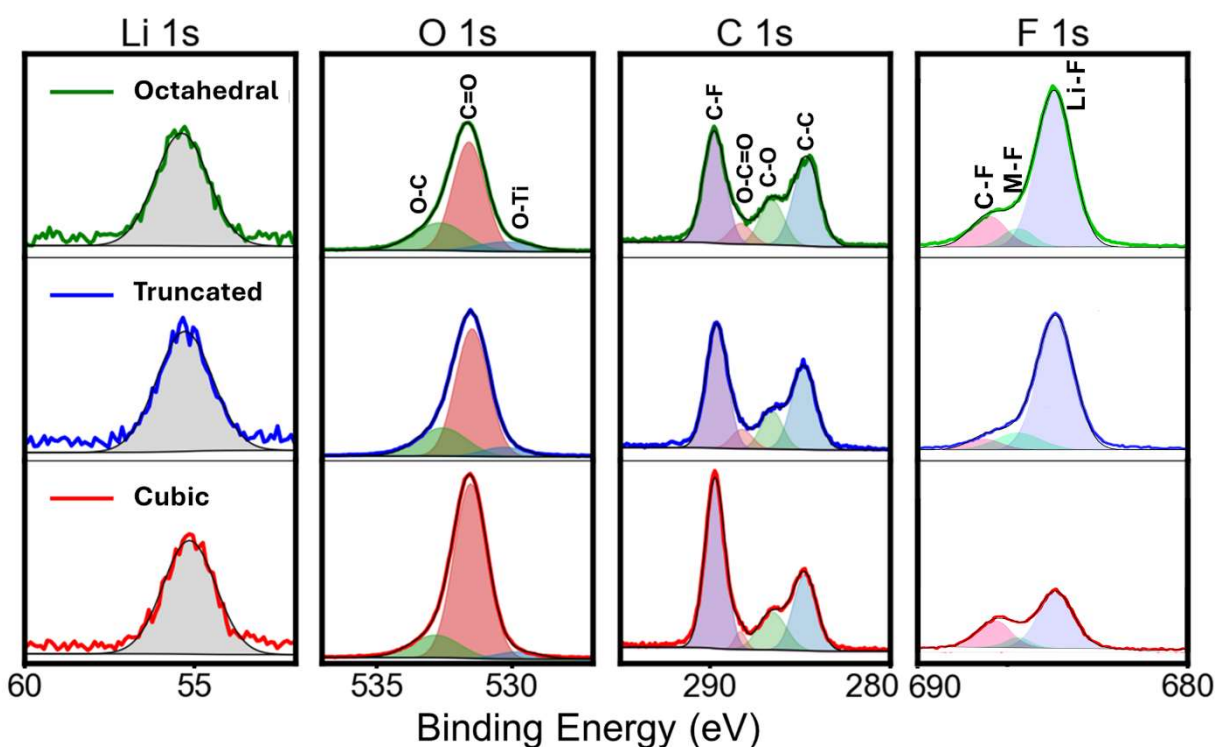


Fig. 9. Post-mortem XPS of (a) Octahedral, (a) Cubic, and (c) Truncated samples after 100th cycle.

The morphology dependence of LiF formation requires a mechanistic explanation. For transition-metal oxides it has been reported that LiF forms rapidly upon initial contact with typical carbonate electrolytes and can dominate the nascent interphase, with little detectable Li_2CO_3 at early times⁶⁹. In the presence of residual water, PF_6^- undergoes hydrolysis to produce species such as $\text{PF}_5\text{H}_2\text{O}$, PF_5OH^- , PF_4OH^- , POF_3 , HPO_2F_2 , and free F^- , which then enter the electrolyte^{70, 71}. Transition-metal-oxide surfaces exposed to

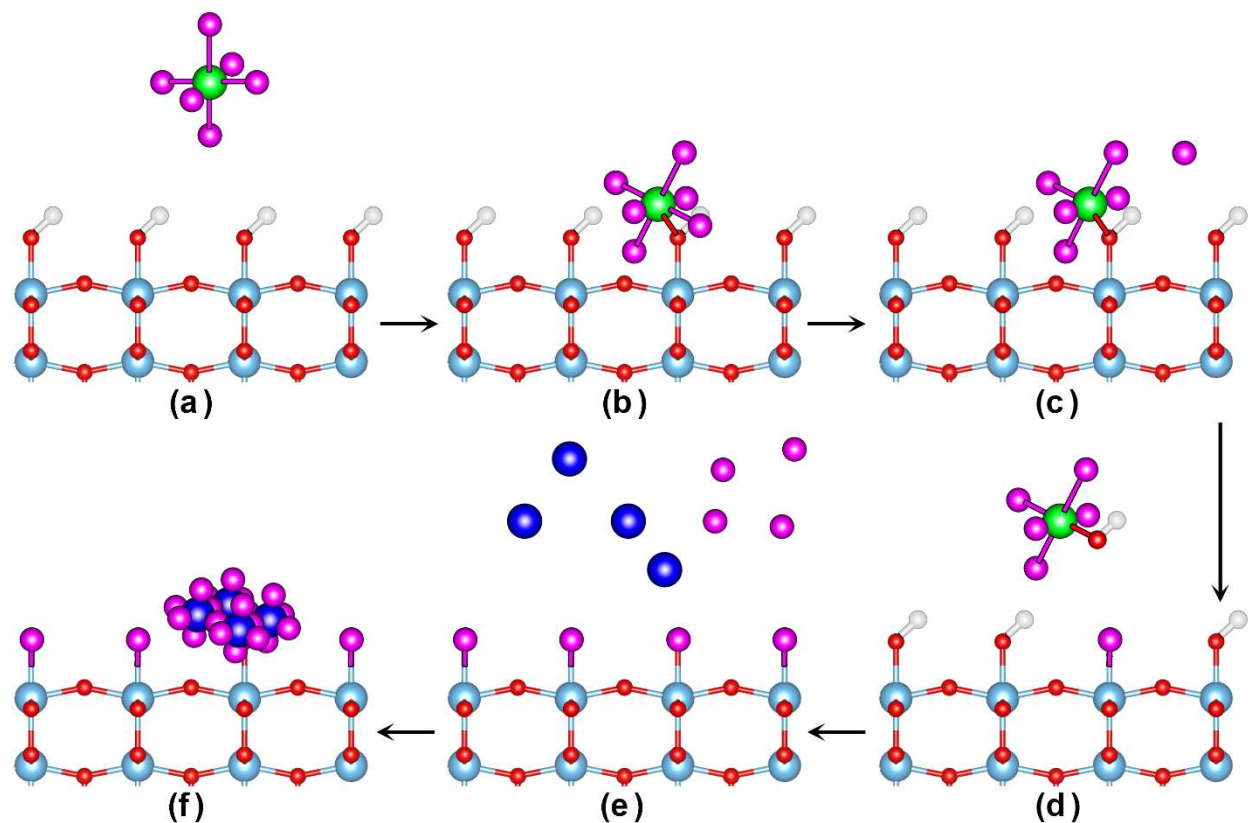
air are readily hydroxylated; these surface –OH groups can promote analogous PF_6^- hydrolysis on the oxide surface, liberating F^- and oxygenated fluorophosphate fragments.

Once generated, F^- has two principal fates at the electrode surface. First, in the absence of strongly coordinating surface functionality, F^- may chemisorb to Ti sites. This adsorption is spontaneous and the Ti–F surface bond is reported to be thermally stable below $\sim 360\text{ K}$ ⁷². Density-functional theory (DFT) calculations indicate that adsorption is energetically preferred at undercoordinated Ti sites (five-coordinate, Ti(5c)) relative to fully coordinated (six-coordinate, Ti(6c)) sites⁷³. Moreover, facet-dependent energetics influence Ti–F bond strengths: the {001} surface is predicted to bind F more strongly (lower energy) than the {101} surface, rendering Ti–F bonds on {001} facets more stable (Scheme 1. (a-d)). By contrast, the weaker Ti–F interaction on {101} facets increases the likelihood of F^- release from the surface.

The second fate of liberated fluoride is precipitation with Li^+ to form LiF. Our data indicate that {001} facets which form stable Ti–F bonds are rapidly passivated (stabilization occurs almost immediately), whereas {100} facets require a finite number of cycles (~ 10 cycles in our measurements) to reach a stabilized state. Facets that are less able to form strong, stable Ti–F bonds—here exemplified by {101}—therefore continue to produce mobile F^- that combines with Li^+ to yield progressively greater LiF deposition over cycling Scheme 1. (e-f). This mechanistic sequence accounts for the morphology-dependent LiF accumulation observed in our XPS and post-mortem analyses.

Collectively, our multi-technique characterization demonstrates that TiO_2 performance as a Li-ion intercalation electrode is inherently “multi-faceted”, governed principally by (i) intercalation geometry and kinetics, (ii) facet-dependent surface stability, and (iii) particle size (surface-to-volume) effects. These parameters are coupled: surface orientation controls the ease and directionality of Li^+ insertion, we find the {001} facets to afford the most favourable initial intercalation kinetics, but once Li^+ enters the lattice the bulk crystal remains chemically and mechanically robust over long cycling. Surface chemistry dictates parasitic pathways, high-energy facets such as {001} and {100} promote rapid early electrolyte decomposition that, paradoxically, produces a fast passivating response (Ti–F formation) and limits subsequent Li-side SEI growth, whereas {101} facets are less able to form stable Ti–F complexes and consequently sustain continued F^- release and progressive LiF precipitation. Particle size modulates these effects: smaller particles increase the absolute area for parasitic reactions, and thus are more susceptible to pore occlusion, yet they also enhance ionic access and rate capability; an optimum size/facet balance is therefore required to maximize practical performance. Taken together, these insights provide a coherent design rationale; namely, engineering an electrode microstructure that combines facets and dimensions to (a) promote rapid, perpendicular Li^+ access, (b) enable controlled, self-limiting surface passivation, and (c) minimize long-

term pore clogging by LiF, which should be broadly applicable when designing improved intercalation electrodes for both anodes and cathodes.



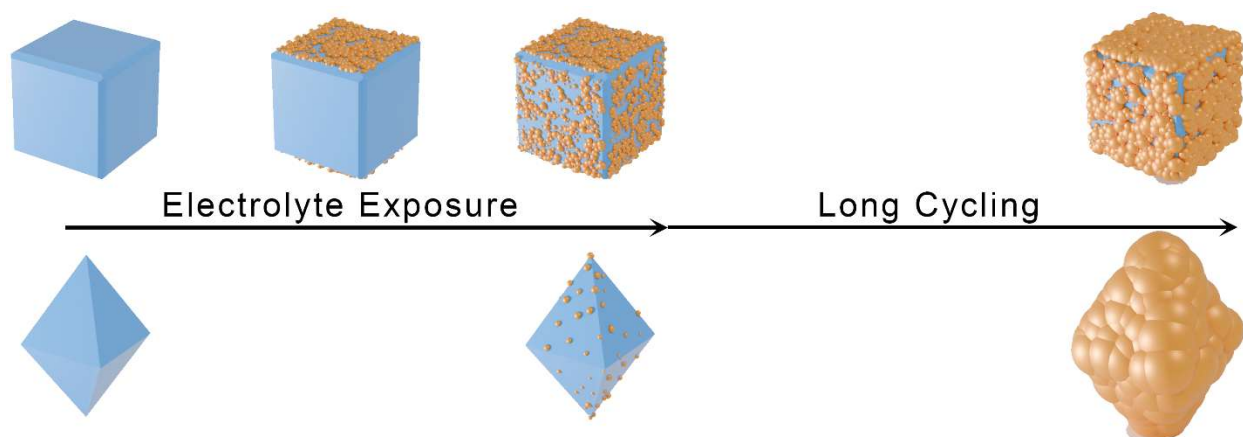
Scheme 1. Possible pathways for PF_6^- decomposition and surface stabilization. (a–d) Surface stabilization — PF_6^- hydrolysis/decomposition yields F^- that chemisorbs to undercoordinated Ti sites to form stable Ti–F surface complexes (rapid passivation, favored on $\{001\}$ facets). (e–f) LiF precipitation — persistent F^- combines with Li^+ to precipitate porous LiF, leading to progressive surface deposition, pore occlusion and transport degradation (favored on $\{101\}$). (Ti: light blue, O: red, H: white, P: green, F: purple, Li: dark blue)

4. Conclusions

This work demonstrates that TiO_2 electrode performance is governed by an interplay of facet chemistry, surface reaction pathways, and particle size rather than bulk crystallinity alone. Cubes with $\{100\}$ facets enable faster, more perpendicular Li^+ insertion and correspondingly higher apparent diffusion and superior rate capability, but they also with $\{001\}$ facets drive an early, rapid parasitic decomposition that critically can be self-limiting via formation of stable Ti–F surface functional groups (Scheme 2, upper path). By

contrast, {101}-rich surfaces are less able to stabilize fluoride at the surface, sustain continued F^- release and progressive LiF precipitation (Scheme 2, lower path), and therefore promote pore occlusion, increased pore resistance and long-term diffusivity loss; particle size amplifies these effects (smaller particles: greater surface area and faster kinetics, but greater susceptibility to clogging).

These mechanistic insights point to concrete design rules: engineer facet exposure to combine fast, perpendicular Li^+ access with a propensity for controlled, self-limiting passivation; optimize particle size to balance short diffusion lengths against excessive reactive surface area; and employ surface coatings or electrolyte formulations that suppress long-range F^- migration and LiF accumulation. Methodologically, cycle-resolved inefficiency analysis (CCIE) coupled with EIS and surface spectroscopy (XPS) provides a compact, diagnostic framework to link kinetic signatures to specific surface chemistries. More broadly, recognizing that a facet's electrochemical “fingerprint” is dynamic under cycling offers a practical pathway to rationally design high-rate, long-lived intercalation electrodes across diverse material systems.



Scheme 2. Behavior of TiO_2 particles bearing high-energy ($\{001\}$, $\{100\}$) versus low-energy ($\{101\}$) facets upon electrolyte exposure and after extended cycling: high-energy facets undergo rapid, self-limiting surface stabilization (Ti-F formation) while low-energy facets promote sustained F^- release and progressive LiF deposition that occludes pores and degrades transport.

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