Na uptake at TiO₂ anatase surfaces under electric field control: A first-principles study

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Na-ion batteries (NIBs) are promising devices for large-scale energy-storage facilities. Nanostructured TiO₂ is an efficient NIB negative electrode, showing good cycling performance and rate capability, but its activity depends on the crystalline facets exposed by anatase nanoparticles. Hence, we propose here a DFT+U study of Na⁺ adsorption and insertion at (101), (100) and (001)-TiO₂ surfaces under the influence of external electric fields, which are simulated by adding a sawtooth-like electrostatic potential to the bare ionic potential. We find that field polarization affects Na⁺ uptake as well as titania electronic features, promoting redox processes within Ti sublattice, as in battery charge/discharge cycling. Our results highlight the high-energy (001) surface to be the most active, for both directions of external fields, proving its activity to be exerted reversibly. Besides further insights, these outcomes pave the route for further exploration and design of electrode materials by simulation of battery in operando conditions.

Introduction

Na-ion batteries (NIBs) are attracting great interest in both academic and industrial research along with the ever-growing demand for sustainable and viable energy-storage solutions [1–3]. Lithium scarce availability and consequent high costs call for new affordable materials for large-scale applications [4–6]. Post-lithium batteries based on cheap and widespread raw materials are foreseen to boost the transition to a sustainable society, with potential applications in smart grid facilities integrated to renewable energy conversion plants and even electric transportation [7–11]. The similar operating principles with state-of-the-art Li-ion batteries (LIBs) have encouraged great advances in research and development of NIBs, but still the quest for different constituent materials is a major concern. While helping in the diffusion through liquid electrolytes, the large Na⁺ radius hinders a convenient reversible intercalation into the structure of the commonly adopted electrodes. In this context, the rational optimization of advanced electrode materials is at the forefront in energy research and their thorough design at the nanoscale has promoted higher reversible capacity, enhanced rate capability, and prolonged durability [12, 13]. On one hand, research on cathode materials relies on the identification of cheap and structurally stable positive electrodes operating at voltage values in the order of 4.5 V vs. Na⁺/Na (or even above), since it is the cathode that mainly affects the battery performance and manufacturing costs [11, 14]. State-of-the-art positive electrodes usually contain rare elements, such as first- and second-row transition metals, that are largely sought as high-voltage redox couples, but still raise the battery price [15, 16]. To this end, Mn- and Fe-rich cathode chemistry offers a means of doing away with Co, by far the most expensive battery material [17, 18]. On the other hand, the development of efficient anodes requires the pursuit for good Na⁺ hosts with suitable structures to reversibly accommodate the large Na⁺ cation [19, 20]. Among many investigated systems, titanium dioxide (TiO₂) represents a viable choice for the overall balance of performance, stability, and cost. This versatile functional material finds applications in several energy conversion technologies, from solar cells to water splitting photocatalysis and batteries [21–24]. Titania-based materials have been widely studied and tested in Li-based cells with remarkable electrochemical performances almost comparable to graphitic systems [25–28]. Still, combination with carbonaceous materials (e.g.,...
graphene, mesoporous carbon, carbon nanotubes) is shown to sensibly improve electronic conductivity [29, 30], while nano-engineering strategies can enable short ion diffusion pathways at the large electrode/electrolyte contact area which favor diffusion kinetics [31]. Recently, significant efforts have been devoted to scaling up nanostructured TiO₂-based materials as NIB negative electrodes [32–41]. Several experimental investigations have highlighted the morphology-dependent performance of anatase electrodes employed in Na cells [40, 41]. In particular, lattice terminations exposed on the surface of TiO₂ nanoparticles (NPs) show different activity, with the (100) and (001) facets being much more effective than the most stable (101) one [41]: the pseudo-capacity behavior observed for anatase NPs exposing different crystal facets suggests that the (101), (100) and (001) surfaces act as intercalation sites for Na⁺. This means that the sodiation process relies on the anode capability to accommodate the ions within the lattice structure, that is the insertion at the subsurface. In this perspective, the surface activity plays a direct role toward the interaction not only at Na-TiO₂ interface, but also on a subsurface level. To the best of our knowledge, previous theoretical attempts focusing on the bare adsorption model have failed in explaining the anatase sodiation mechanism, with the surface activity being badly predicted ((100) > (001) [42]). When modeling the charge/discharge process in a Na-ion battery, the ability of TiO₂ to host the Na⁺ inside the crystalline lattice is of paramount importance and should not be neglected. Most of theoretical studies have addressed the Na⁺ insertion energetics to structural and electronic features of bulk anatase [40, 43, 44]. However, the key role of Na/TiO₂ interface and related interactions that are established upon electrode charging can be clearly evinced. In a first attempt to provide a reliable model for Na⁺ insertion through anatase surfaces, we have recently described the underlying mechanism and explained the surface activity: crystalline facets act as intercalation sites and their different behavior can be ascribed to a convenient accommodation of Na⁺ without significant lattice distortion for the (100) surface, and to an easy insertion through the subsurface layer favored by a large lattice window for the (001) termination [45]. Despite being clear and conclusive, this model still lacks some elements that can be of major importance when modeling the materials behavior under battery operating conditions. The in-depth understanding of electrochemical reactions occurring at electrode surfaces relies on accurate computational methods able to describe and predict the undergoing processes at in operando conditions.

To this end, we here investigate the Na⁺ adsorption and insertion processes at the (101), (100) and (001) surface terminations under the influence of an external electric bias, thus modeling the charge/discharge conditions. Our aim is to unveil how the direction and the intensity of the applied field can affect the adsorption and insertion energetics as well as the structural and electronic properties of anatase surfaces. Although the chemical interactions and electronic features may be sensibly affected when an external bias comes into play, the effect of electric fields is commonly neglected in standard DFT simulations. With the modern theory of polarization, the Berry-phase approach has allowed to include an applied external field in periodic DFT calculations [46–49]. This method is designed for 3D periodic systems and is well-suited for studying the bulk materials processes and the properties derived from dipole moments and polarization [50–54]. Furthermore, AIMD simulations with Berry-phase method have been used to understand how water dissociation and proton conductivity are affected by applied fields [55, 56]. For 2D periodic materials, the inclusion of a sawtooth potential has enabled the study of field effects on oxygen vacancy migration at the anatase surface and Cu migration in SiO₂ cristobalites [57, 58]. The idea is to simulate an electric field along the longitudinal axis and perpendicular to the interface plane, by using a sawtooth-like potential added to the bare ionic potential [59]. The sawtooth potential spans throughout the slab cell with a constant slope, and then reaches the middle of the vacuum region where the slope is reversed to ensure periodicity. This is equivalent to the application of a constant electric field to the main region of the periodic cell. This approach has allowed to model the interface between a solid-state electrolyte, i.e., Li₄N₃Clₓ, and the Li metal under charging conditions [60], and to study to what extent an external electric field can affect the separation of photogenerated electron–hole pairs in semiconductors [61]. Following the computational approach pioneered by Selloni and coworkers [57], we hereby simulate the electric field in the direction perpendicular to the anatase surface models by means of the sawtooth-like potential approach [59]. Our investigation points out that Na⁺ insertion can be favored when the electric field is opposite to the z-axis and that the Ti⁴⁺/³⁺ redox couple involved during the Na⁺ insertion is affected by the presence of this electrostatic field. These outcomes can improve the current understanding of electrochemical reactions at NIB electrode surfaces and will be helpful toward further methodological implementations of bias effects into electrode/electrolyte interface models.

**Results and discussion**

In this work, we aim at investigating electric field effects on the Na⁺ uptake mechanism at TiO₂ anatase interface. Our approach builds up on previous results from our group and on the pioneering work by Selloni et al. for including the sawtooth-like potential in our calculations [45, 57]. First, we address Na adsorption on the most stable and reactive TiO₂ anatase surfaces, i.e., (101), (100) and (001) (see Figure S1 for slab models and Table S1 for structural details in the Supporting Information), under the influence of external electric...
fields, that hereafter are named positive and negative depending on whether it lies in the same or opposite direction of the z-axis, giving a positive or negative slope, respectively (\(\vec{F}\) and \(-\vec{F}\), see Scheme 1).

Figure 1 shows the minimum-energy structures of Na-adsorbed states (i.e., Na\(_{\text{OUT}}\)) on top of TiO\(_2\) anatase surfaces and corresponding structural arrangements induced by positive/negative electric fields of equal strength (\(|\vec{F}| \times 10^3 = 5\) Ha and \(-5\) Ha). For all the surfaces, Na–O bonds undergo elongation when a positive field is applied, while shrinking under negative field. As highlighted in Fig. 1 (framed boxes, blue, green, and violet for (101), (100) and (001) surfaces, respectively), the effect of positive field is most relevant on the (001) surface, with a Na–O bond variation of \(\sim 0.6\) Å versus 0.4 Å and 0.2 Å for (101) and (100) cases, respectively. Conversely, negative field effect on the (001) surface can be almost neglected, while only slightly affecting the other surfaces with \(\sim 0.1\) Å distortion of Na–O bonds. This trend is respected when an intermediate strength field (\(|\vec{F}| \times 10^3 = 2.5\) Ha, \(-2.5\) Ha) is considered (Figure S2). It is worth to mention that Na adsorption on (001) surface termination leads to two identical geometries at \(|\vec{F}| \times 10^3 = 2.5\) Ha and \(-5\) Ha, suggesting that in this case the structure reaches an asymptotic value at high fields. Thus, compared to the unperturbed systems, Na adsorption sites are located further from the surface under positive field and closer in the case of negative field.

For all these minimum-energy structures, we compute the adsorption energies, \(E_{\text{ads}}\) as:

\[
E_{\text{ads}} = E_{\text{NaOUT}} - E_{\text{slab}} - \frac{1}{2} E_{\text{Na}} \tag{1}
\]

where \(E_{\text{NaOUT}}\), \(E_{\text{slab}}\) and \(E_{\text{Na}}\) are the total energies of Na\(_{\text{OUT}}\) states, pristine surface slabs at \(|\vec{F}| \times 10^3 = 5\text{Ha}, \text{2.5Ha, 0Ha,} -\text{2.5Ha or} -\text{5Ha}\), and metallic sodium (the \textit{bcc} 2-atoms cell is taken as reference [20]), respectively. Corresponding energies are plotted in Fig. 2(a) and listed in Table S2. We have also evaluated the adsorption as referred to the total energy of a Na atoms-containing 10-layer slab model with 15 Å of vacuum to account for field effects (\(E_{\text{Naout}}\)). As shown in Table S2, adsorption energetics is not affected. The adsorption energy trend at zero-field confirms our previous results with \(E_{\text{ads}}\) (001) > (101) > (100) [45]. The positive field [right-hand side graphs in Fig. 2(a)] favors sodium adsorption, with \(E_{\text{ads}}\) lowered by 0.4/0.6 eV, while the negative field [left-hand side graphs in Fig. 2(a)] leads to a 0.2 eV increase in adsorption energies. To unveil the origin of field effects on Na adsorption, we dissect the energy contributions in terms of interaction (\(E_{\text{int}}\)) and distortion energies (\(E_{\text{dis}}\)) defined as:

\[
E_{\text{int}} = E_{\text{NaOUT}} - E_{\text{surf}} - E_{\text{NaOUT}} \tag{2}
\]

\[
E_{\text{dis}} = E_{\text{NaOUT}}^{\text{surf}} - E_{\text{surf}} \tag{3}
\]

where \(E_{\text{surf}}^{\text{NaOUT}}\) and \(E_{\text{surf}}\) are the total energies of each surface slab at the Na-adsorbed geometry (i.e., Na\(_{\text{OUT}}\)) and in their minimum-energies, respectively, while \(E_{\text{NaOUT}}\) is the total energy of the sodium atom at the Na\(_{\text{OUT}}\) geometry, computed at each field strength and polarization. The resulting values are plotted in panels b and c of Fig. 2. It is clear that the three TiO\(_2\) surfaces exhibit different trends: the polarization of the electric field does not affect the Na-TiO\(_2\)(001) interaction [Fig. 2(b), violet line], which is equally lowered at both positive and negative fields, and thus the more favorable \(E_{\text{ads}}\) at positive field can be ascribed to the smaller lattice distortion [Fig. 2(c), violet line]; in the case of (101) and (100) facets, highly stabilizing interactions are observed at positive fields [Fig. 2(b), blue and green lines], which compensate the increased distortion [Fig. 2(c), blue and green lines] and explain the more convenient \(E_{\text{ads}}\). We also address to what extent these structural rearrangements within the TiO\(_2\) lattice are induced by the Na adsorption process or the electric field itself. To this end, it is possible to calculate the surface distortion upon the application of the external field, thus
examining structural modifications due to the bias itself: $E_{\text{dis}}(F)$ can be calculated as

$$E_{\text{dis}}(F) = E_{\text{surf}}(F) - E_{\text{surf}}(F_0)$$

where $E_{\text{surf}}(F)$ and $E_{\text{surf}}(F_0)$ are the total energies of the surface slabs in their minimum-energy structures at positive/negative fields ($F, \frac{\vec{F}}{x 10^3} = 5\text{Ha}, 0\text{Ha}, -5\text{Ha}$) and zero-field ($F_0, \frac{\vec{F}}{x 10^3} = 0\text{Ha}$), respectively. From the overall negative $E_{\text{dis}}(F)$ values plotted in Fig. 2(d), we can conclude that all the surfaces undergo a slight stabilization regardless of the field polarization, and so the different distortion must be related to lattice arrangements aiming to accommodate a Na atom on a given surface step. In principle, it is possible to evaluate a further energy decomposition analysis, by calculating the distortion energy required to rearrange the atomic coordinates from the zero-field geometry to the ones obtained from positive/negative fields (without applying the bias). In this way, the mere structural effects induced by the field are taken into account. We obtain comparable contributions among all the surfaces and fields (in the range of $\sim 0.1$ eV), while a higher value is obtained in case of NaOUT-(001) at positive field (0.25 eV). As a measure of the energy amount for readjusting the Na+ position at the new adsorption sites, the higher distortion observed for NaOUT-(001) at positive field can be ascribed to a larger rearrangement of the Na+ as shown in Fig. 1, the NaOUT-(001) at positive field is the one displaying the Na further from the surface). Overall, these results highlight that positive fields would favor adsorption process on each surface, due to the enhanced Na-TiO$_2$ interactions at the (101) and (100) surfaces and to a lower lattice distortion at (001) surface. Noteworthy, the lowest-energy NaOUT states at positive fields are stabilized in adsorption sites lying further from the surface.

Figure 1: Na-adsorbed states (NaOUT) on top of (from left to right) (101), (100) and (001) TiO$_2$ surfaces obtained at PBE + U level of theory with (from top to bottom) positive, zero and negative field. The field strength is defined using the slope, $F$, (in Hartree), of the sawtooth potential (from top to bottom $\frac{\vec{F}}{x 10^3} = 5\text{Ha}, 0\text{Ha}, -5\text{Ha}$). Color code: Na (yellow), Ti (cyan) and O (red).
The field effects on the electronic structure of Na\textsuperscript{OUT}-TiO\textsubscript{2} interface are analyzed in terms of charge density difference (e.g., CD plot) between positive/negative and zero-field. Figure 3 shows that positive and negative fields lead to electron loss (orange surfaces) and gain (green surfaces), respectively, corresponding to oxidation and reduction of Ti atoms. This is also confirmed by variation of average magnetization and Löwdin charges on Ti atoms within the two topmost layers, as reported in Table 1. Despite being very small due to the strong hybridization of Ti \textit{d} and O \textit{p} states (see PDOS in Figure S4) leading to charges far away from the ionic limits, these variations can still prove how the field affects the electronic structure. From the overall analysis on the electronic structure (CD plots in Fig. 3 and Table 1), we can qualitatively infer that the electron density accumulation/depletion occurring under the influence of negative/positive field only involve Ti atoms within the two topmost layers (i.e., Ti-2L), suggesting a reducing/oxidizing effect depending on the field polarization. This result is very relevant for NIB operating condition, since the Ti\textsuperscript{4+}/\textsuperscript{3+} redox couple is directly involved during Na\textsuperscript{+} intercalation reaction \[62, 63\]. The field polarization may be easily associated to the battery cycling reactions, with the sawtooth-like potential showing a positive slope being representative of a discharge process, i.e., desodiation from the anode coupled to Ti oxidation occurring in the low-voltage range. Further details on the electronic structure of Na\textsuperscript{OUT} systems can be found in the Supporting Information and consist of CD plots and projected density of states (PDOS, see Figures S3 and S4). All the surface terminations show a common pattern of charge transfer from Na atom to Ti sublattice, with a weaker interaction detected at positive field. The adsorption of a Na atom always leads to population of states at the edge of TiO\textsubscript{2} conduction band, which reveals that our model is representative of a Na\textsuperscript{+} interacting with a n-type semiconductor, as desired for the NIB electrode. In principle, the electric field may also perturb the electronic structure of pristine TiO\textsubscript{2}, i.e., before Na adsorption. Again, we decompose this analysis by reporting the CD plots for the clean anatase surfaces upon application of the field (see Figure S5). However, we do not observe any charge density variation, and so we can assess the charge transfer to be determined by Na adsorption at a given field polarization.

Recent studies have revealed that a bare adsorption model is not reliable for describing the electrochemical activity of Na\textsuperscript{+} at TiO\textsubscript{2} NP surfaces \[45\]. The subsurface insertion model seems to be more effective to this purpose and the surface lattice windows...
have been pointed out as a limiting factor for Na$^+$ uptake [45]. Here, we explore the field effects in Na-inserted states at the subsurface layer of TiO$_2$ surfaces, i.e., Na$^{IN}$, and we evaluate the change of surface lattice windows as function of field values. In this case, insertion energetics is essentially unchanged with the applied field and the corresponding structural modifications are neglectable, probably because of a higher screening exerted by the surface layer (see Figure S6 in SI). However, because of field effects on $E_{ads}$, the IN–OUT energy gap is affected. Figure 4 illustrates the energy gap decreases upon the presence of a negative field (see red lines and corresponding values in Fig. 4), suggesting that the negative polarization can facilitate Na$^+$ insertion through TiO$_2$ NPs, the larger effect being detected at the (001) surface. As a matter of fact, the area exposed by the surface lattice windows and defined at Na$^{OUT}$ states gets larger upon the effect of negative field (see Figure S7 in SI). Again, the intrinsic structural properties featured by the anatase surfaces can explain the origin of different activity toward Na$^+$ uptake, even under the influence of an external electric field. Comparison of the resulting $\Delta E$ reveals that Na insertion is more likely to occur at the (001) surface. This termination is predicted to be the most active when either a positive or negative field is applied, showing the lowest energy variations compared to the others. These findings are in line with previous results, with $\Delta E = E_{IN} - E_{OUT}$ (100) > (101) > (001), and also highlight that the high efficiency of (001)-terminated NPs is exerted reversibly upon charge/discharge cycling. Indeed, field polarization can be thought as the direction of the external bias that is present during battery cycling, with the negative one that favors Na intercalation and leads to the reduction of Ti sublattice being representative of the charge process, i.e., sodiation reaction.

### Conclusions

This work presents the first-principles characterization of Na$^+$ adsorption and insertion through TiO$_2$ anatase crystal facets, that are the (101), (100) and (001) surfaces, under the influence of an external electric field. Usually, electric field effects are neglected in common DFT simulations of electrode interface. Following our previous study on the sodiation of TiO$_2$ anatase, we hereby provide further insights on the underlying mechanism for sodium adsorption and insertion when an external field is applied.
electric bias is applied. The field is simulated in the direction perpendicular to the surface by adding a sawtooth-like potential to the bare ionic potential, according to computational approaches reported in the recent literature. We show how the inclusion of two opposite polarizations can lead to opposite effects. In particular, we find that positive/negative fields: (i) stabilize Na\textsubscript{OUT} sites further/closer to the surface; (ii) favor the adsorption on the surface/insertion at the subsurface layer; (iii) promote the oxidation/reduction of Ti sublattice, and thus can account for the desodiation/sodiation of the anodic electrode occurring upon discharge/charge. Overall, our study clearly shows the reliability of electric fields-based DFT calculations in the description of electrode surface processes under applied bias, paving the route for further theoretical investigations on the external bias effects for electrode–electrolyte interfacial properties and processes. From the energy-storage perspective, our approach will be useful to improve the current understanding of electrochemical reactions at NIB negative electrodes and will help the rational design of new effective anodes by modeling realistic in operando conditions.

Methods and computational details

For all the calculations, we use spin-polarized density functional theory DFT + U methods \cite{64, 65} within the supercell approach that employs periodic boundary conditions (PBC) and plane-wave (PW) basis sets, as implemented in Quantum Espresso \cite{66}. We use the generalized gradient approximation (GGA) for the exchange–correlation density functional as proposed by Perdew, Burke and Ernzerhof (PBE), plus an effective $U_{\text{eff}} = 3.3$ eV parameter for $d$ electrons of Ti atoms \cite{67–69}. The projector-augmented wave (PAW) potentials are taken from QE repository \cite{70, 71} and the wave functions (augmented charge density) are expanded in plane waves with a 70 (280) Ry cutoff. We apply the surface-slab approach to build up the structural models for (101), (100) and (001) surfaces by cleaving up the optimized bulk structure along those lattice planes and then introducing a 15 Å vacuum slab along the c direction \cite{72}. Our surface models consist of 10-layer slabs containing 40 formula units (120 atoms) (Figure S1 and Table S1). We use the $2 \times 2 \times 1$ \textit{k}-point sampling based on a Monkhorst–Pack scheme and take into account dipole correction as implemented in QE \cite{73}. The external electric field in the direction perpendicular to the slabs is simulated by adding a sawtooth-like potential to the bare ionic potential \cite{57, 59, 74}. We reverse the slope of the sawtooth potential ($F$) in a small region (~ 0.5 $a_0$) in the middle of the vacuum to ensure periodicity. Calculations are performed with $|F| \times 10^3 = 5$ Ha (blue lines), and negative field, $|F| \times 10^3 = -5$ Ha (red lines).

![Figure 4:](https://example.com/figure4.png) Insertion and adsorption energetics for Na\textsubscript{IN} and Na\textsubscript{OUT} states at TiO\textsubscript{2} surfaces calculated at PBE + U level of theory. All the energy values, $E_{\text{ads}}$, are referred to Na-adsorbed on (100) surface with zero-field (yellow box). Color code: zero-field (black lines), positive field, $|F| \times 10^3 = 5$ Ha (blue lines), and negative field, $|F| \times 10^3 = -5$ Ha (red lines).

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Declarations

Conflict of interest The authors declare no competing financial interest.

Data availability

Data will be made available upon reasonable request.

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Supplementary Information

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