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First-principles investigation of aluminum intercalation and diffusion in TiO_2 materials: Anatase versus rutile

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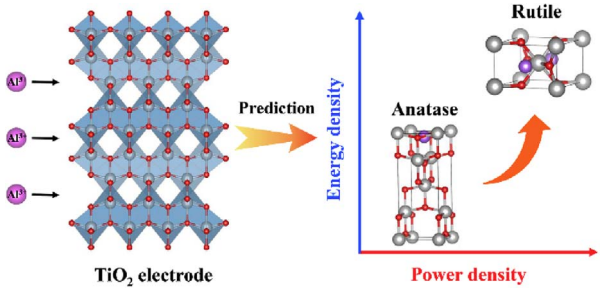
HIGHLIGHTS

- Intercalation of aluminum into TiO_2 electrode is evaluated theoretically.
- Energy capacity and diffusion rate are examined in two common TiO_2 polymorphs.
- TiO_2 rutile represents a better candidate than anatase as electrode materials.

GRAPHICAL ABSTRACT



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ABSTRACT

Aluminum-ion batteries, emerging as a promising post-lithium battery solution, have been a subject of increasing research interest. Yet, most existing aluminum-ion research has focused on electrode materials development and synthesis. There has been a lack of fundamental understanding of the electrode processes and thus theoretical guidelines for electrode materials selection and design. In this study, by using density functional theory, we for the first time report a first-principles investigation on the thermodynamic and kinetic properties of aluminum intercalation into two common TiO_2 polymorphs, i.e., anatase and rutile. After examining the aluminum intercalation sites, intercalation voltages, storage capacities and aluminum diffusion paths in both cases, we demonstrate that the stable aluminum intercalation site locates at the center of the O_6 octahedral for TiO_2 rutile and off center for TiO_2 anatase. The maximum achievable Al/Ti ratios for rutile and anatase are 0.34375 and 0.36111, respectively. Although rutile is found to have an aluminum storage capacity slightly higher than anatase, the theoretical specific energy of rutile can reach 20.90 Wh kg^{-1}, nearly twice as high as anatase (9.84 Wh kg^{-1}). Moreover, the diffusion coefficient of aluminum ions in rutile is 10^{-9} $cm^2 s^{-1}$, significantly higher than that in anatase (10^{-20} $cm^2 s^{-1}$). In this regard, TiO_2 rutile appears to be a better candidate than anatase as an electrode material for aluminum-ion batteries.

1. Introduction

The rapidly increasing penetration of renewable energies has urged the development of efficient battery storage techniques. Although lithium ion batteries (LIBs), currently enjoying a great market success in consumer electronics, have attracted the most attention as a candidate

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Nomenclature

a, b, c	Lattice parameters (Å)
d	Hopping distance of ions (Å)
D	Diffusion coefficient ($cm^2\ s^{-1}$)
E	Internal (potential) energy (kJ mol^{-1})
ΔE_a	Activation energy (kJ mol^{-1})
F	Faraday's constant, 96485 A s mol^{-1}
g	Geometric factor
G	Gibbs free energy (kJ mol^{-1})
k_B	Boltzmann constant, 1.38×10^{-23} J K^{-1}
M_V	Molar volume (L mol^{-1})
M_W	Molar weight (g mol^{-1})
T	Temperature (K)
ν	Atomic vibration frequency (s^{-1})
$V(x)$	Average voltage (V)
x	Molar fraction
x_{max}	Theoretical maximum concentration
z	Number of electrons involved in electrode

Greek symbols

α, β, γ	Lattice parameters (deg)
ε_M	Gravimetric energy density (Wh kg^{-1})
ε_V	Volumetric energy density (Wh L^{-1})

for transport and grid applications [1–4], the high cost, lithium availability and safety concerns associated with LIBs necessitate the development of alternative battery solutions. Aluminum-ion batteries that rely on the principle of reversible intercalation of chloroaluminate ($[Al_xCl_y]^-$) or aluminum ions have emerged as a promising post-lithium solution since 2010 when they were invented [5]. The use of aluminum instead of lithium in rocking chair batteries offers many advantages, including (i) potentially low cost due to the abundance of aluminum resources, (ii) improved safety by eliminating the need for flammable organic electrolytes, and (iii) high theoretical capacity due to the trivalent nature of aluminum ions.

Identifying suitable electrode materials with high energy and power capabilities lies at the heart of the R&D of aluminum ion batteries. In contrast to monovalent lithium ions, the high valence state of aluminum ions together with their small ionic radii (54 pm for Al^{3+} versus 76 pm for Li^+) make their intercalation into a host crystal structure challenging [6–8]. Among different potential electrode materials, TiO_2, a widely studied material for electrochemical lithium storage, is of particular interest due to its attractive features such as good structural stability, low toxicity, high safety and low cost. It has been reported that eight types of crystal structures exist for TiO_2 material [9]. In 2012, Liu et al. [10] demonstrated for the first time the reversible intercalation of Al^{3+} ions into TiO_2 with anatase TiO_2 nanotube arrays in an aqueous $AlCl_3$ electrolyte. They confirmed that the redox of Ti^{4+}/Ti^{3+} was responsible for the reversible storage of Al^{3+} ions in TiO_2. A specific capacity of 75 mAh g^{-1} at a current density of 4 mA g^{-1} was reported in their study. The Al^{3+} storage performance was shown to be significantly improved by employing black anatase TiO_2 nanoleaves [11] and high-surface-area anatase TiO_2 nanospheres [12], which respectively achieved 278 mAh g^{-1} (at 50 mA g^{-1}) and 183 mAh g^{-1} (at 50 mA g^{-1}). Very recently, we demonstrated good aluminum storage performance with nanosized rutile TiO_2 [13]. It is noted that aluminum intercalation in TiO_2 has been evidenced only in aqueous electrolytes. So far, no evidence of aluminum intercalation has been reported for non-aqueous electrolytes. Despite these encouraging achievements, there is still a lack of atomic-level understanding of aluminum intercalation processes in TiO_2 materials. In particular, the thermodynamic limit and atomistic mechanisms of Al^{3+} diffusion in TiO_2 are generally unclear.

This study therefore presents a density-functional-theory (DFT) study of aluminum intercalation into two common TiO_2 polymorphs, i.e., anatase and rutile, with the aim of providing atomic-level insights into the electrode processes. The thermodynamic and kinetic behaviors associated with the two different TiO_2 polymorphs are thoroughly studied and carefully compared, which can lead to a better understanding of the battery performance and guide on further materials design for aluminum ion batteries.

2. Modelling and computational methods

All calculations were carried out by using periodic DFT within the Vienna ab initio simulation package (VASP) [14,15]. VASP provides an iterative solution of the Kohn-Sham equations of DFT upon a plane wave basis, wherein the inner cores and electron-ion interactions are described with pseudopotentials through the projected augmented wave (PAW) method [16,17]. A plane-wave basis set with a cutoff energy of 500 eV was used to expand the eigenstates of the electron wave functions. The calculation systems were established with periodic boundary conditions. A supercell containing 96 atoms with $2 \times 2 \times 4$ unit cells was modelled for TiO_2 rutile whereas a supercell containing 108 atoms with $3 \times 3 \times 1$ unit cells was modelled for TiO_2 anatase [18,19]. To maximize computational efficiency while not affecting the calculation accuracy, a minimal Monkhorst-Pack $5 \times 5 \times 2$ k-point grid was used to sample the Brillouin zones for our structure calculations. The convergence criterion for the electronic self-consistent cycle was fixed at 0.01 meV per cell. Full relaxation of all atomic positions was performed until the forces on all atoms were less than 0.1 meV $Å^{-1}$ per cell for assuring geometrical and energetic convergence. The climbing-image nudged elastic band (CI-NEB) method [20] was used to calculate the minimum energy pathways (MEPs) and the energy barriers for aluminum diffusion in the TiO_2 materials.

2.1. Aluminum intercalation voltage

It has been proposed in the previous research [10] that the electrochemical aluminum intercalation into TiO_2 follows the below reaction:

$$TiO_2 + x\ Al\ (metal) \leftrightarrow Al_xTiO_2, \quad (1)$$

where x is the molar fraction of aluminum. The average voltage of (1) for a composition range between 0 and x, $V(x)$ (V), can be therefore expressed as [21]:

$$V(x) = -\Delta G/xzF, \quad (2)$$

where ΔG (kJ mol^{-1}) is the Gibbs free energy change due to the aluminum intercalation, F ($=96485$ A s mol^{-1}) is the Faraday constant, and z is the number of the charge transferred during the reaction per mole reactant ($z = 3$). Under ambient conditions, ΔG can be approximated with the internal (potential) energy change (ΔE) by neglecting the contribution from the configurational and vibrational entropy change due to the intercalation. While the entropy contribution can be calculated through the vibrational frequencies [22], it has been reported that this contribution is overall small compared to the internal energy at room temperatures (typical working conditions of aqueous aluminum-ion batteries), and thus can be ignored [21,23]. The change of internal energy is given by:

$$\Delta E = E(Al_xTiO_2) - E(TiO_2) - xE(Al), \quad (3)$$