Probing Capacity Trends in MLi$_2$Ti$_6$O$_{14}$ Lithium-Ion Battery Anodes Using Calorimetric Studies

K. Jayanthi, Anshuman Chaupatnaik, Prabeer Barpanda, and Alexandra Navrotsky*

ABSTRACT: Due to higher packing density, lower working potential, and area specific impedance, the MLi$_2$Ti$_6$O$_{14}$ (M = 2Na, Sr, Ba, and Pb) titanate family is a potential alternative to zero-strain Li$_4$Ti$_5$O$_{12}$ anodes used commercially in Li-ion batteries. However, the exact lithiation mechanism in these compounds remains unclear. Despite its structural similarity, MLi$_2$Ti$_6$O$_{14}$ behaves differently depending on charge and size of the metal ion, hosting 1.3, 2.7, 2.9, and 4.4 Li per formula unit, giving charge capacity values from 60 to 160 mAh/g in contrast to the theoretical capacity trend. However, high-temperature oxide melt solution calorimetry measurements confirm strong correlation between thermodynamic stability and the observed capacity. The main factors controlling energetics are strong acid–base interactions between basic oxides MO$_2$, Li$_2$O and acidic TiO$_2$, size of the cation, and compressive strain. Accordingly, the energetic stability diminishes in the order Na$_2$Li$_2$Ti$_6$O$_{14}$ > BaLi$_2$Ti$_6$O$_{14}$ > SrLi$_2$Ti$_6$O$_{14}$ > PbLi$_2$Ti$_6$O$_{14}$. This sequence is similar to that in many other oxide systems. This work exhibits that thermodynamic systematics can serve as guidelines for the choice of composition for building better batteries.

INTRODUCTION

Lithium-ion batteries (LIBs) are the currently favored power sources for portable applications such as electric vehicles and electronic products. Most commercial LIBs work via reversible intercalation of lithium ions between a (mixed) transition metal oxide cathode and a layered graphite anode. For more than 30 years since the inception of LIBs by SONY (Tokyo, Japan) in the 1990s, graphite remains the most widely used and optimized anode material due to its high theoretical capacity (380 mAh/g) and low Li insertion voltage (ca. 0.2 V) while maintaining an intercalation mechanism, which guarantees structural integrity and long cycle life. Nevertheless, the graphite anode has several issues, such as solvent-dependent stability, large volume change, large irreversible capacity loss (ICL) from solid electrolyte interphase (SEI) formation (below 0.8 V), and fire risk due to lithium plating during overcharge or higher currents some of which directly stem from its low voltage performance.

In this context, the zero-strain spinel Li$_4$Ti$_5$O$_{12}$ anode operating at flat and higher voltage (1.55 V vs Li, 175 mAh/g) was introduced and is commercially preferred over graphite in applications requiring fast charging and safety. Additionally, Li$_2$Cr$_2$Ti$_6$O$_{14}$ similar to Li$_4$Ti$_5$O$_{12}$ spinel synthesized at 800 °C exhibits large charge capacity, good cycle stability, superior rate performance, and outstanding electrochemical kinetics. When cycled at 200 mA/g, it displays a high initial reversible capacity of 146.6 mAh/g and retains a considerable capacity of 130.8 mAh/g after 300 cycles. Among other Ti-based electrode materials, MLi$_2$Ti$_6$O$_{14}$ (M = 2Na, Sr, Ba, and Pb) shows lower voltage (1.28–1.42 V vs Li), low area specific impedance, and higher packing density than Li$_4$Ti$_5$O$_{12}$ and has a high theoretical capacity (220–282 mAh/g) for redox activity of all six Ti (Figure 1i).

The MLi$_2$Ti$_6$O$_{14}$ series exhibit open channels enabling reversible Li$^+$ insertion in vacant sites like 8c, 4a, and 4b of the orthorhombic framework (Cmca). However, the observed capacity trend in this series does not follow the theoretical capacity trend. Previous studies identified crystallographic origins underlying the low capacity of the monovalent member (M = 2Na) vs the divalent members (M = Ba, Sr, and Pb). However, currently there is no explanation of the anomalous trend of the observed capacity in the isostructural divalent members—BaLi$_2$Ti$_6$O$_{14}$ (2.7 Li) < SrLi$_2$Ti$_6$O$_{14}$ (2.9 Li) < PbLi$_2$Ti$_6$O$_{14}$ (4.4 Li)—where PbLi$_2$Ti$_6$O$_{14}$ is opposite to the theoretical capacity trend.

We take a new approach to understand the electrochemical property trend in this isostructural MLi$_2$Ti$_6$O$_{14}$ series from their relative thermodynamic stabilities, attempting to elucidate the structure–property relationships in this family of materials. High-temperature oxide melt solution calorimetry is an established methodology to measure the thermodynamic stabilities of oxide and nonoxide systems. Recently, Abramchuk et al. used this method to investigate the thermodynamic stability and its role in the mechanism of ionic

Received: September 2, 2022
Accepted: October 26, 2022
transport in the NASICON-type solid-state electrolyte Li$_{1+x}$Al$_x$Ti$_2$O$_7$ (PO$_4$)$_3$. They demonstrated a strong correlation between the energetic stability and ionic conductivity in LATPs with a pronounced change in the trends with composition. In the present work, we employ high-temperature oxide melt solution calorimetry to systematically assess the thermodynamic stability of MLi$_2$Ti$_6$O$_{14}$ (M = Na, Sr, Ba, and Pb), which provides insights into observed differences in the capacity. We found a strong correlation between the thermodynamic stability and reversible lithium insertion in MLi$_2$Ti$_6$O$_{14}$ anode materials and explain the trend in observed capacity. This work reflects the acid-base energetic contributions in this class of anode materials.

**EXPERIMENTAL SECTION**

**Synthesis and Electrochemistry.** MLi$_2$Ti$_6$O$_{14}$ was synthesized by a two-step solution combustion method. Metal nitrates as oxidizers (O) and glycine as fuel (F) were taken in a 1:1 ratio to ensure maximum exothermicity. Lithium nitrate (LiNO$_3$, Sigma-Aldrich, 99%), sodium nitrate (NaNO$_3$, SD Fine, 99.5%), barium nitrate (Ba(NO$_3$)$_2$, Sigma-Aldrich, >99%), lead nitrate (Pb(NO$_3$)$_2$, SD Fine, 99.5%), and strontium nitrate (Sr(NO$_3$)$_2$, Sigma-Aldrich, 99%) were used. Titanium (Ti$^{4+}$) ions were sourced from freshly prepared titanyl nitrate (TiO(NO$_3$)$_2$ as it is unstable). This was made by simultaneous hydrolysis—nitration of titanium isopropoxide (C$_{12}$H$_{25}$O$_7$Ti, Sigma-Aldrich, 97%) in isopropyl alcohol.

![Figure 1](https://pubs.acs.org/journal/acsodf/article/2021/acsomega.2c05701)
The mixture was heated to less than 150 °C to remove water and form a thick solution, which was reheated at 500 °C to trigger combustion. The resulting white intermediate powder was ground, pelletized, and annealed in air at 900 °C for 1 min to 2 h. The phase purity of combustion prepared MLi₂Ti₆O₁₄ samples was verified from powder X-ray diffraction patterns (2θ range = 10–50°, step size = 0.026° s⁻¹) obtained using a PANalytical X’Pert Pro X-ray diffractometer having a Cu-Kα source (λ = 1.54 Å). Rietveld refinement was done using the GSAS program.28 The structures were illustrated using the VESTA software.29

The surface morphology of the powders was characterized using a scanning electron microscope having a LaB₆ field emission source (Carl Zeiss ULTRASS FESEM, 5 kV) and using a transmission electron microscope (FEI Tecnai F20 STwin, 200 kV). TG-DSC measurements were performed using a Setaram LABSYS EVO instrument. 25 mg of the powdered sample was pressed into a pellet, placed in a Pt crucible, and heated from 30 to 800 °C (10 °C/min) under a N₂ flow (20 mL/min). A buoyancy correction was performed with an empty crucible prior to the experiment. The pristine powder was ground with carbon (Super P, Sigma-Aldrich, >99%) in an Ar-filled glovebox (MBraun LABStar). Whatman GF/C glass fiber was used as the separator and 1 M LiPF₆ in 1:1:3 v/v % of ethylene carbonate/propylene carbonate/dimethyl carbonate (EC/PC/DMC) (chameleon reagent) was used as the electrolyte. The cells were cycled between 2 V to 1 or 0.5 V at C/20 and 50 mA/g current using a Neware BTS-4000 battery cycler to ensure we reach the maximum specific capacity values for each of the materials, which can then be rationalized with the thermodynamic trend.

High-Temperature Oxide Melt Solution Calorimetry.

High-temperature oxide melt solution calorimetry was performed using a Setaram AlexSYS Tian-Calvet twin micro-calorimeter using methods standard to our laboratory and described previously.20-22 This calorimeter allows the direct determination of the enthalpy of formation (ΔH°f) of multicomponent compounds from their binary oxides. In a typical experiment, ~5 mg of the MLi₂Ti₆O₁₄ sample was pelletized and dropped from ambient temperature into a calorimeter at 800 °C containing the solvent molten sodium molybdate (3Na₂O·4MoO₃) in a platinum crucible. The measured enthalpy of drop solution (ΔHd) is the sum of the sample heat content from ambient temperature to 800 °C and its heat of solution in the solvent at 800 °C. At least 8–10 experiments were done per sample, and the results are reported as average values with error being two standard deviations of the mean. The calorimetry glassware was flushed with oxygen gas at a flow rate of 65 mL/min to maintain a constant atmosphere, and the solvent was bubbled with the same gas at 5 mL/min to remove liberated evolved gases, aid dissolution, and prevent local saturation of the solvent. The calorimeter was calibrated using the heat content of 5 mg of pellets of α-Al₂O₃ (99.997%). The details of the calorimeter and procedures have been described previously.20-22

RESULTS AND DISCUSSION

Structure and Electrochemical Performance. The combustion synthesized MLi₂Ti₆O₁₄ powders were found to be phase pure from Rietveld refinement (Figure 1a–d and Tables S1–S4, Supporting Information). The powders were well crystallized into primary particles of about 1 micron, which agglomerated to a porous network (Figure 1e,f). The crystal structure is orthorhombic (symmetry: Cmca), containing a three-dimensional network of TiO₆ octahedral units. Two edge-shared units along the a-axis stitch the infinite c-axis directed edge-shared units in a ladderlike way. The ladders form a sheet in the b,c plane. In the sheet, inside each c-directed ladder, there is an empty tunnel where structural lithium ions sit in tetrahedral sites with adjacent octahedral sites free. This sheet is three units thick along the a-axis and is glued to other sheets via larger M ions which populate the interlayer partially (M = Sr, Ba, and Pb) or completely (M = 2Na). One unit of MLi₂Ti₆O₁₄ can host up to six lithium atoms, for complete reduction of Ti⁴⁺ to Ti³⁺, offering a theoretical capacity of about 240 mAh/g depending on the atomic weight of M (Table 1). The mechanism of lithium insertion is unclear, and only about 75% of theoretical capacity has been attained.

Table 1. Space Group, Charge Capacity, and Li Uptake per Formula Unit of the MLi₂Ti₆O₁₄ Titanates

| anode material | space group | charge capacity (mAh/g) | operating voltage (V) vs Li | Li uptake (per fa.) |
|----------------|-------------|------------------------|-----------------------------|--------------------|
| Na₂Li₂Ti₆O₁₄   | Cmca        | 62                     | 1.28                        | 1.32               |
| SrLi₂Ti₆O₁₄    | Cmca        | 111                    | 1.42                        | 2.74               |
| BaLi₂Ti₆O₁₄    | Cmca        | 125                    | 1.38                        | 2.85               |
| PbLi₂Ti₆O₁₄    | Cmca        | 162                    | 1.35                        | 4.40               |

MLi₂Ti₆O₁₄ is the lightest among MLi₂Ti₆O₁₄ (M = 2Na, Sr, Ba, and Pb) and so it is expected to have the highest theoretical capacity of 282 mAh/g for six Ti redox (Figure 1i). However, due to the geometrical constraints, it cannot insert more than two Li (62 mAh/g, 1.3 Li) as the vacant 11-atomic site is the lightest among MLi₂Ti₆O₁₄ (M = 2Na, Sr, Ba, and Pb) and so it is expected to have the highest theoretical capacity of 282 mAh/g for six Ti redox (Figure 1i). However, due to the geometrical constraints, it cannot insert more than two Li (62 mAh/g, 1.3 Li) as the vacant 11-atomic site is the lightest among MLi₂Ti₆O₁₄ (M = 2Na, Sr, Ba, and Pb) and so it is expected to have the highest theoretical capacity of 282 mAh/g for six Ti redox (Figure 1i)–m). Furthermore, even the divalent counterparts with half-filled interlayers are space limited as they reversibly allow only four lithium ions (instead of six) via reduction of four out of six Ti ions. Lithium ions (de)insert from 1.2 to 1.5 V in the system, with each member showing its signature (de)insertion voltage (Figure 1n–q). The observed charge capacity is in the order BaLi₂Ti₆O₁₄ (111 mAh/g, 2.7 Li) < SrLi₂Ti₆O₁₄ (125 mAh/g, 2.9 Li) < PdLi₂Ti₆O₁₄ (162 mAh/g, 4.4 Li). While a slightly higher observable capacity in the Sr analog compared to Ba is in line with the trend in their theoretical capacity, the reason why PdLi₂Ti₆O₁₄ shows the largest capacity and uptakes significantly more lithium despite being the heaviest is highly intriguing. To address this question, we embark on investigating the thermodynamic stability in this family of compounds.

Thermodynamic Studies. Thermochemical data are sensitive to the crystal structure, phase, and chemical purity of the sample. PXRD and TG-DSC measurements were performed before the calorimetric measurement to detect any possible contamination/decomposition and check for adsorbed...
water on the sample due to exposure in the ambient atmosphere prior to calorimetric experiments. Samples were phase pure as shown in Figure 1a–d, and TGA measurements detected no mass loss, confirming there was no adsorbed water on the samples.

The drop solution enthalpy ($\Delta H_{ds}$) and formation enthalpy from oxides ($\Delta H^\circ_{f,ox}$) of MLi$_2$Ti$_6$O$_{14}$ ($M = \text{Na, Sr, Ba, and Pb}$) as a function of Li uptake per unit formula are shown in Table 2 and Figure 2a,b. The enthalpy of drop solution of PbO, SrO, and BaO is obtained from the drop solution enthalpy ($\Delta H_{ds}$) of MLi$_2$Ti$_6$O$_{14}$ ($M = \text{Na, Sr, Ba, and Pb}$) is calculated from the thermochemical cycles in Table 3.

Table 2. Drop Solution Enthalpies ($\Delta H_{ds}$) in 3Na$_2$O·4MoO$_3$ at 800 °C and Formation Enthalpies ($\Delta H^\circ_{f,ox}$) at 25 °C of MLi$_2$Ti$_6$O$_{14}$ ($M = \text{Na, Sr, Ba, and Pb}$) Titanates

| Sample          | $\Delta H_{ds}$ (kJ/mol) | $\Delta H^\circ_{f,ox}$ (kJ/mol) |
|-----------------|--------------------------|----------------------------------|
| Na$_2$Li$_2$Ti$_6$O$_{14}$ | 502.41 ± 0.35(8)         | −333.32 ± 4.91                   |
| Ba$_2$Li$_2$Ti$_6$O$_{14}$ | 506.75 ± 0.57(8)         | −323.54 ± 3.44                   |
| Sr$_2$Li$_2$Ti$_6$O$_{14}$ | 498.16 ± 0.68(8)         | −260.65 ± 3.15                   |
| Pb$_2$Li$_2$Ti$_6$O$_{14}$ | 508.46 ± 0.46(8)         | −157.81 ± 2.54                   |
| Li$_2$O         | −77.21 ± 2.44$^{22}$     |                                   |
| Na$_2$O         | −195.90 ± 4.23$^{22}$    |                                   |
| Ti$_2$O         | 73.70 ± 0.39(6)$^{25}$   |                                   |
| SrO            | −127.48 ± 1.84$^{22}$    |                                   |
| BaO            | −181.22 ± 2.32$^{22}$    |                                   |
| PbO            | −14.34 ± 0.38 (6)$^{22}$ |                                   |
| CO$_2$         | 37.40                    |                                   |

$^{22}$This work. The value is the mean of the number of experiments indicated in parentheses; two standard deviations are given as errors.

PbO, SrO, and BaO is obtained from the drop solution enthalpy of lead oxide and strontium carbonate (SrCO$_3$ and BaCO$_3$) at 800 °C using the thermochemical cycle in Tables S5 and S6 (Supporting Information). The enthalpies of drop solution of Li$_2$O, Na$_2$O, and TiO$_2$ are taken from our previous measurements. The formation enthalpy ($\Delta H^\circ_{f,ox}$) of MLi$_2$Ti$_6$O$_{14}$ ($M = \text{Na, Sr, Ba, and Pb}$) is calculated from the thermochemical cycles in Table 3.

The $\Delta H_{ds}$ for lithium titanates is endothermic ranging from 498.16 ± 0.68 to 508.46 ± 0.46 kJ/mol, and $\Delta H^\circ_{f,ox}$ is exothermic ranging from −333.32 ± 4.91 to −157.81 ± 2.54 kJ/mol, confirming that these materials are thermodynamically stable. $\Delta H_{ds}$ does not follow any regular trend but $\Delta H^\circ_{f,ox}$ is inversely proportional to lithium uptake in MLi$_2$Ti$_6$O$_{14}$ (Figure 2b). The least stable PbLi$_2$Ti$_6$O$_{14}$ ($\Delta H^\circ_{f,ox} = −157.81 ± 2.54$ kJ/mol) intercalates the most lithium (4.4 Li), followed by SrLi$_2$Ti$_6$O$_{14}$ ($\Delta H^\circ_{f,ox} = −260.65 ± 3.15$ kJ/mol, 3.08 Li), then BaLi$_2$Ti$_6$O$_{14}$ ($\Delta H^\circ_{f,ox} = −323.54 ± 3.44$ kJ/mol, 2.47 Li), while the most stable NaLi$_2$Ti$_6$O$_{14}$ ($\Delta H^\circ_{f,ox} = −333.32 ± 4.91$ kJ/mol) inserts the least lithium (1.32 Li). Factors such as size of the metal ion, geometrical and compressive strains, and “acid–base” interaction explains their stability trend.

The energetics of the ternary oxide formation is dominated by the difference in the acid–base character of the cations. Binary oxides are classified as acidic, basic, or amphoteric. Smith’s table$^{26}$ expresses all metal oxides in terms of acidity and the enthalpies of formation from binary oxides for lithium titanates change linearly with acidity. This validates the trends observed in the formation enthalpies, and in turn the lithium uptake (Figure 2c). The highly exothermic heats of formation reflect strong acid–base interactions among the MO, and Li$_2$O (basic oxides) with TiO$_2$ (a somewhat acidic oxide). The basic binary oxides MO and Li$_2$O interact with the acidic TiO$_2$ to form the MLi$_2$Ti$_6$O$_{14}$ structure. Alkali metal oxides exhibit greater basic character followed by alkaline earth metal oxides, among the divalent oxides those of larger cations are more basic compared to lighter cations, the order of basicity for MO is Na$_2$O > BaO > SrO. $^{31}$ Thus, the acid–base interaction between MO, Li$_2$O, and TiO$_2$ which stabilizes the structure most strongly in Na$_2$Li$_2$Ti$_6$O$_{14}$ followed by BaLi$_2$Ti$_6$O$_{14}$, then SrLi$_2$Ti$_6$O$_{14}$. This explains the trend observed in the $\Delta H^\circ_{f,ox}$ Na$_2$Li$_2$Ti$_6$O$_{14}$ > BaLi$_2$Ti$_6$O$_{14}$ > SrLi$_2$Ti$_6$O$_{14}$. This correlation is consistent with the dominance of the acid–base chemistry in phase stability, as seen in trends of enthalpies of formation in

---

*Figure 2. (a) Dissolution enthalpy (b) formation enthalpy vs reversible Li uptake (per formula unit) in the lithium titanates, and (c) enthalpies of formation from oxides for lithium titanates as a function of acidity based on Smith’s scale of acidity for alkali, alkali-earth, and lead oxides.*$^{22}$
Table 3. Thermodynamic Cycles Used to Calculate Formation Enthalpies (ΔH°f,m) of MLi₂Ti₆O₁₄ at 25 °C

| reaction                                                                 | ΔH (kJ/mol) |
|--------------------------------------------------------------------------|-------------|
| MLi₂Ti₆O₁₄(s,25°C) → MO(solv,25°C) + Li₂O(solv,25°C) + 6TiO₂(solv,25°C)     | ΔH₁ = ΔH₂ = 181.22 ± 2.32a |
| Li₂O(solv,25°C) → Li₂O(solv,25°C)                                        | ΔH₁ = 195.90 ± 4.23a |
| Na₂O(solv,25°C) → Na₂O(solv,25°C)                                        | ΔH₁ = 73.70 ± 0.39a |
| TiO₂(solv,25°C) → TiO₂(solv,25°C)                                        | ΔH₁ = 127.48 ± 1.84a |
| SrO(solv,25°C) → SrO(solv,25°C)                                         | ΔH₁ = 143.34 ± 0.38a |
| BaO(solv,25°C) → BaO(solv,25°C)                                         | ΔH₁ = 143.34 ± 0.38a |
| PbO(solv,25°C) → PbO(solv,25°C)                                         | ΔH₁ = 143.34 ± 0.38a |
| MO(solv,25°C) + Li₂O(solv,25°C) + 6TiO₂(solv,25°C) → MLi₂Ti₆O₁₄(s,25°C)  | ΔH₂ = 77.21 ± 2.44a |
| ΔH₂ = ΔH₃(MLi₂Ti₆O₁₄)                                                  | ΔH₁ = 181.22 ± 2.32a |
| ΔH₂ = 195.90 ± 4.23a                                                   | ΔH₁ = 73.70 ± 0.39a |
| ΔH₂ = 127.48 ± 1.84a                                                   | ΔH₁ = 143.34 ± 0.38a |
| ΔH₂ = 143.34 ± 0.38a                                                   | ΔH₁ = 143.34 ± 0.38a |

This work.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c05701.

Rietveld refinement of MLi₂Ti₆O₁₄ (M = Sr, Ba, and 2Na) titanates and thermodynamic cycles used to calculate the drop solution enthalpy (ΔHₘ) of SrO and BaO in sodium molybdate at 800 °C (PDF)

### AUTHOR INFORMATION

#### Corresponding Author

Alexandra Navrotsky — School of Molecular Sciences and Navrotsky Eyring Center for Materials of the Universe, Arizona State University, Tempe, Arizona 85287, United States; orcid.org/0000-0002-3260-0364; Email: Alexandra.Navrotsky@asu.edu

#### Authors

K. Jayanthi — School of Molecular Sciences and Navrotsky Eyring Center for Materials of the Universe, Arizona State University, Tempe, Arizona 85287, United States; Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States; orcid.org/0000-0002-5016-3575

Anshuman Chaupatnaik — Faraday Materials Laboratory, Materials Research Centre, Indian Institute of Science,

---

It can be concluded that there is strong correlation between the thermodynamic stability and the lithium uptake in this class of materials. Strong exothermic acid–base reactions between MO, Li₂O, and TiO₂ result in large exothermic enthalpies of formation, indicating that MLi₂Ti₆O₁₄ are thermodynamically stable. Depending on the nature of acid–base interactions, the stability varies, alkalil metals exhibit greater basic character followed by alkaline earth metal oxides, and among the alkaline earth metal oxides, those of larger cations are more basic compared to lighter cations, and the order of basicity for MO is Na₂O > BaO > SrO. PbO is an amphoteric oxide for which the acid–base interaction is weak compared to alkali or alkaline earth metal oxides. Thus, the thermodynamic stability diminishes in the order Na₂Li₂Ti₆O₁₄ > BaLi₂Ti₆O₁₄ > SrLi₂Ti₆O₁₄ > PbLi₂Ti₆O₁₄ which is directly proportional to the acid–base interactions. The trends in stability also depend on the charge and size of the cation and the compressive strain which are typical for interoxidic compounds. The formation enthalpy in these materials is inversely proportional to the lithium uptake during charge cycles. Least stable PbLi₂Ti₆O₁₄ uptakes most Li (4.4 Li), and the most stable Na₂Li₂Ti₆O₁₄ uptakes least Li (1.3 Li).
Bangalore 560012, India; Chimie du Solide-Energie, UMR 8260, Collège de France, Paris 75001, France

Prabir Barpanda — Faraday Materials Laboratory, Materials Research Centre, Indian Institute of Science, Bangalore 560012, India; Helmholtz Institute Ulm (HIU), Electrochemical Energy Storage, Ulm 89081, Germany; Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Karlsruhe 76021, Germany; orcid.org/0000-0003-0902-3690

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c05701

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

K.J. and A.N. acknowledge the U.S. Department of Energy Office of Basic Energy Sciences, grant DE-SC0021987 for calorimetric measurements and thermodynamic analysis. P.B. is grateful to the Alexander von Humboldt Foundation (Bonn, Germany) for a 2022 Humboldt fellowship for experienced researchers. A.C. is grateful to the Ministry of Human Resource Development (MHRD) and Raman-Charpak Fellowship-2019 by Centre Franco-Indien pour la Promotion de la Recherche Avancée (CEFIPRA) for financial support and Prof. Jean-Marie Tarascon for hosting him at Collège de France, Paris. This manuscript has been authored by UT-Battelle, LLC under Contract No. DEAC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/doe-public-access-plan).

REFERENCES

(1) Goodenough, J. B.; Park, K. K. The Li-ion rechargeable battery: A perspective. J. Am. Chem. Soc. 2013, 135, 1167−1176.

(2) Whittingham, M. S. Electrical energy storage and intercalation chemistry. Science 1976, 192, 1126−1127.

(3) Ohzuku, T.; Iwakoshi, Y.; Sawai, K. Formation of lithium-graphite intercalation compounds in nonaqueous electrolytes and their application as a negative electrode for a lithium ion (shuttlecock) cell. J. Electrochem. Soc. 1993, 140, 2490−2498.

(4) Aurbach, D.; Cohen, Y.; Teller, H. A short review of failure mechanisms of lithium metal and lithiated graphite anodes in liquid electrolyte solutions. Solid State Ionics 2002, 148, 405−416.

(5) Winter, M.; Barnett, B.; Xu, K. Before Li ion batteries. Chem. Rev. 2018, 118, 11433−11456.

(6) Fong, R.; Sacken, U.; Dahn, J. R. Studies of lithium intercalation into carbons using nonaqueous electrochemical cells. J. Electrochem. Soc. 1990, 137, 2009−2013.

(7) Han, J. T.; Huang, Y. H.; Goodenough, J. B. New anode framework for rechargeable batteries. Chem. Mater. 2011, 23, 2027−2029.

(8) Colbow, K. M.; Dahn, J. R.; Haering, R. R. Structure and electrochemistry of the spinel oxides LiTi2O4 and Li4Al3Ti5O12. J. Power Sources 1989, 26, 397−402.

(9) Ohzuku, T.; Ueda, A.; Yamamoto, N. Zero-strain insertion material of Li[(Li1/2Ti1/3)O2 for rechargeable lithium cells. J. Electrochem. Soc. 1995, 142, 1431−1435.

(10) Zaghib, K.; Donthigny, M.; Guerfi, A.; Charest, P.; Rodrigues, I.; Mauger, A.; Julien, C. M. Safe and fast-charging Li-ion battery with long shelf life for power applications. J. Power Sources 2011, 196, 3949−3954.

(11) Liu, S.; Yan, L.; Lan, H.; Yu, H.; Qian, D.; Cheng, X.; Long, N.; Shui, M.; Shu, J. Investigation of Li2Cr2TiO7 as novel anode material for high-power lithium-ion batteries. Ceram. Int. 2017, 43, 7908−7915.

(12) Patoux, S.; Masquelier, C. Lithium insertion into titanium phosphates, silicates, and sulfates. Chem. Mater. 2002, 14, 5057−5068.

(13) Zhu, G.; Wang, Y.; Xia, Y. Ti-based compounds as anode materials for Li-ion batteries. Energy Environ. Sci. 2012, 5, 6652−6667.

(14) Chen, Z.; Belharouak, I.; Yen, Y.-K.; Amine, K. Titanium-based anode materials for safe lithium-ion batteries. Adv. Funct. Mater. 2013, 23, 959−969.

(15) Belharouak, I.; Amine, K. Li2MTiO4 (M = Sr, Ba): New anodes for lithium-ion batteries. Electrochem. Commun. 2003, 5, 435−438.

(16) Dambournet, D.; Belharouak, I.; Amine, K. MLi2TiO4 (M = Sr, Ba, 2Na) lithium insertion titanate materials: A comparative study. Inorg. Chem. 2010, 49, 2822−2826.

(17) Li, P.; Qian, S.; Yu, H.; Yan, L.; Lin, X.; Yang, K.; Long, N.; Shui, M.; Shu, J. PbLi2TiO4: A novel high-rate long-life anode material for rechargeable lithium-ion batteries. J. Power Sources 2016, 320, 45−54.

(18) Dambournet, D.; Belharouak, I.; Ma, J.; Amine, K. Template-assisted synthesis of high packing density SrLi2TiO4 for use as anode in 2.7-V lithium-ion battery. J. Power Sources 2011, 196, 2871−2874.

(19) Yi, T.-F.; Zhu, Y.-R.; Tao, W.; Luo, S.; Xie, Y.; Li, X.-F. Recent advances in the research of MLi2TiO4 (M = 2Na, Sr, Ba, Pb) anode materials for Li-ion batteries. J. Power Sources 2018, 399, 26−41.

(20) Naivrotsky, A. Progress and new directions in high temperature calorimetry. Phys. Chem. Miner. 1997, 2, 89−104.

(21) Naivrotsky, A. Progress and new directions in high temperature calorimetry revisited. Phys. Chem. Miner. 1997, 24, 222−241.

(22) Naivrotsky, A. Progress and new Directions in calorimetry: A 2014 perspective. J. Am. Ceram. Soc. 2014, 97, 3349−3359.

(23) Abramchuk, M.; Voskanyan, A. A.; Arinicheva, Y.; Lilova, K.; Subramani, T.; Ma, Q.; Dashjav, E.; Finsterbusch, M.; Naivrotsky, A. Energetic stability and its role in the mechanism of ionic transport in NASICON-type solid-state electrolyte Li1+xAl1−xTiO3. J. Phys. Chem. Lett. 2021, 12, 4400−4406.

(24) Chung, S. L.; Wang, C. M. Solution combustion synthesis of TiO2 and its use for fabrication of photoelectrode for dye-sensitized solar cell. J. Mater. Sci. Technol. 2012, 28, 713−722.

(25) Von Dreele, R. B.; Larson, A. C. General structure analysis system (GSAS). Los Alamos Natl. Lab. Rep. LAUR 2004, 748, 86−748.

(26) Momma, K.; Izumi, F. VESTA: a three-dimensional visualization system for electronic and structural analysis. J. Appl. Crystallogr. 2008, 41, 653−658.

(27) Yang, S.; Andreko, A.; Riman, R.; Naivrotsky, A. Thermochimistry of sodium rare earth ternary fluorides, NaREF3, Acta Mater. 2021, 220, No. 117289.

(28) Hayun, S.; Tran, T. B.; Lian, J.; Fuentes, A. F.; Naivrotsky, A. Energetics of stepwise disordering transformation in pyrochlores, RE2Ti2O7 (RE = Y, Gd and Dy). Acta Mater. 2012, 60, 4303−4310.

(29) Naivrotsky, A. Repeating patterns in mineral energetics. Am. Mineral. 1994, 79, 589−605.

(30) Smith, D. W. An acidity scale for binary oxides. J. Chem. Educ. 1978, 64, 480−481.

(31) David Jackson, S.; Hargreaves, J. S. Metal Oxide Catalysis; Wiley: Germany, 2008; Vol. I, ch. 3, pp 167−168.

(32) Sahu, S. K.; Zlotnik, S.; Naivrotsky, A.; Vilarinho, P. M. Thermodynamic stability of lead-free alkali niobate and tantalite Perovskites. J. Mater. Chem. C 2015, 3, 7691−7698.
(33) Nhu, S.; Navrotsky, A. Energetics of formation of alkali and ammonium cobalt and zinc phosphate frameworks. *J. Solid State Chem.* **2008**, *181*, 20–29.

(34) Navrotsky, A. Thermochemical studies of nitrides and oxynitrides by oxidative oxide melt calorimetry. *J. Alloys Compd.* **2001**, *321*, 300–306.

(35) Shvareva, T. Y.; Fein, J. B.; Navrotsky, A. Thermodynamic properties of uranyl minerals: constraints from calorimetry and solubility measurements. *Ind. Eng. Chem. Res.* **2012**, *5*, 607–613.

(36) Wu, L.; Koryttseva, A.; Groß, C. B. M.; Navrotsky, A. Thermochemical investigation of lithium borate glasses and crystals. *J. Am. Ceram. Soc.* **2019**, *102*, 4538–4545.

(37) Roy, B. N.; Navrotsky, A. Thermochemistry of charge-coupled substitutions in silicate glasses: The systems $M_{\text{in}}^{\text{III}}\text{AlO}_2\text{SiO}_3$ ($M = \text{Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Pb}$). *J. Am. Ceram. Soc.* **1984**, *67*, 606–610.