High-Capacity, Low-Voltage Titanate Anodes for Sodium-Ion Batteries

Project ID # BAT428

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6/25/2021

2021 DOE Vehicle Technologies Office Annual Merit Review

Overview

Timeline

- Project start date 10/1/2018
- Project end date 9/30/2021
- Percent complete 90 %

Budget

- Total project funding
  - DOE share 100 %
  - Contractor share N/A
- Funding for FY2020 $ 300 k
- Funding for FY2021 $ 200 k

Barriers and Technical Targets

- Barriers addressed
  - Supply issues with Li and Co
  - Cost
  - Safety and rate capability

Partners

- LBNL
- Project lead: Marca M. Doeff

Relevance

- Na-ion batteries are a possible drop-in replacement for Li-ion batteries
  - Similarity in concept means we can leverage engineering knowledge (closest "beyond lithium ion" system to commercialization).
  - Co-free cathodes are available for Na-ion batteries (the ethics of Co mining are an issue for Li-ion batteries, as well as its cost).
  - Na-ion anodes do not require Cu current collectors, can use Al. This lowers cost and alleviate concerns about Cu, another strategic metal.
  - Na-ion electrolytic solutions are generally 10-15% more conductive than their Li-ion analogs. Can use less electrolyte salt (a cost savings), and/or design cells with thicker electrodes without compromising the energy/power ratio, another cost-savings.
  - State-of-the-art Na-ion batteries exceed energy densities of Li-ion batteries with $LiFePO_4$ cathodes.

- Need better anodes for Na-ion batteries
  - Safety concerns with the hard carbon anodes currently used.
  - Energy density is dependent on anode material (we have good cathodes).
  - Goal of this project is to investigate the possibility of titanate anodes, another goal is to study electrolytes that can enable these electrodes.

Milestones-FY2020

Milestone	Type	Date/Status
SEI studies and electrolytes (XPS, XAS, ATR-FTIR)	Milestone	Q1/Completed
Synthesize lepidocrocite titanates	Milestone	Q2/Completed
Select best electrolyte solution	Milestone	Q3/Completed
Go/no go decision on sodium nonatitanate	Go/no go	Q4/Go decision, goal for capacity of 200 mAh/g was attained.

Any proposed future work is subject to change based on funding levels

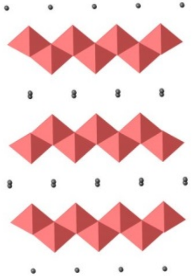
Milestones-FY2021

Milestone	Type	Date/Status
Characterize lepidocrocite titanates	Milestone	Q1/Completed
Optimize electrodes (carbon content, binder, etc.)	Milestone	Q2/Completed
Assemble, test and study full cells	Milestone	Q3/Planned
Go/no go decision on lepidocrocite titanates	Go/no go	Q4/Planned, stop if material doesn’t achieve goals.

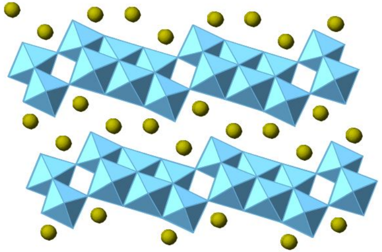
Any proposed future work is subject to change based on funding levels

Approach

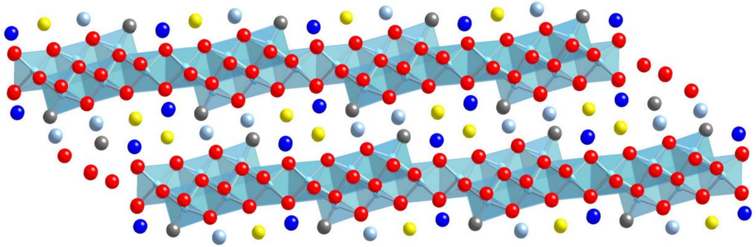
- ☐ Candidate titanate anode materials are synthesized and studied.
- ☐ Several techniques are used to understand their sodium insertion mechanisms and their interfacial properties. These include *in situ* synchrotron XRD, XAS, XPS and other spectroscopic techniques.



Lepidocrocite-type
Step-size=1



$Na_2Ti_3O_7$
Step-size=3



Sodium nonatitanate ($NaTi_3O_6OH$)
Step-size=6

Background

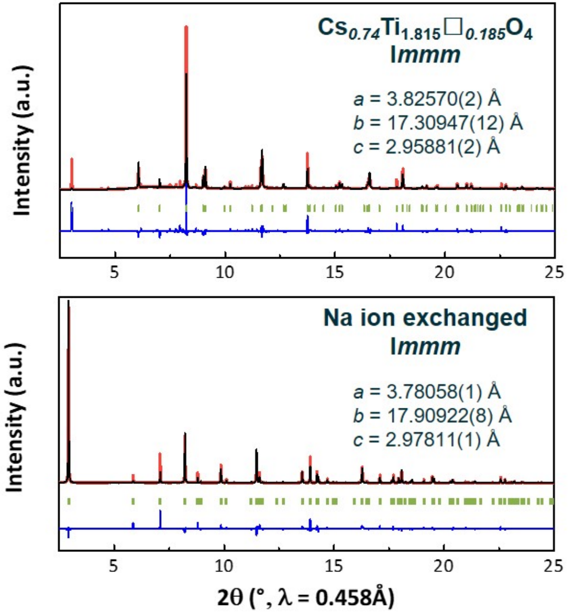
- ☐ There are several corrugated layered Na-Ti-O titanates that can reversibly insert Na ions.
  - We have chosen 3 to study initially (see Approach) based on their structural similarities but quite different electrochemical behavior.
    - **Lepidocrocite-structured titanates.** Step size=1. Variable compositions, $A_xTi_{2-y}M_yO_4$; A=large cation, M=vacancy, Li, Mg, Co, Ni, Fe, Mn, Cu, Zn, etc. Sloping featureless voltage profiles, similar to super-capacitor with $V_{av}\approx0.5V$ *vs.* Na/Na^+. See M. Shirpour, *et al*. Chem. Mater. 2014, 26, 2502.
    - **$Na_2Ti_3O_7$.** Step size=3. Flat voltage profile at ~0.3V *vs.* Na/Na^+. Two-phase behavior. See P. Senguttuvan *et al*. Chem. Mater. 2011, 23, 4109.
    - **"Sodium nonatitanate" $NaTi_3O_6(OH)$.** Step size=6. Sloping featureless voltage profile, similar to supercapacitor with $V_{av}\approx0.3V$ *vs.* Na/Na^+. See M. Shirpour, *et al*. Energy & Environ. Sci. 2013, 6, 2538.

- ☐ Questions we would like to answer
  - Is the electrochemical mechanism of lepidocrocite structured titanates and sodium nonatitanate different from $Na_2Ti_3O_7$ (supercapacitor *vs.* insertion)?
  - If so, why?
  - Can we exploit supercapacitor behavior to improve energy density?
  - How do the step size differences relate to the electrochemistry? Can we design other materials based on the information we obtained?

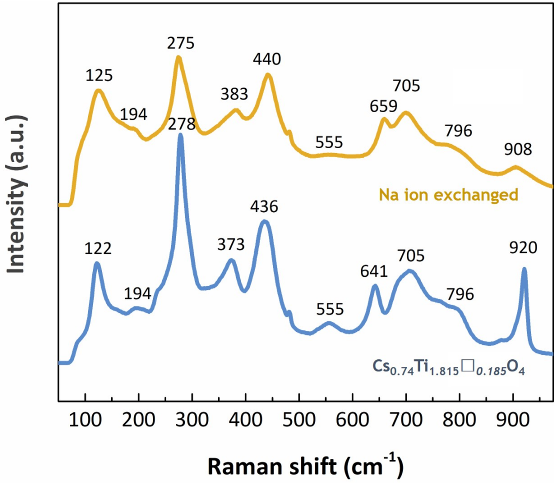
Technical Accomplishments

Characterization of lepidocrocite-structured titanate $Na_xTi_{2-x/4}\square_{x/4}O_4$; x=0.74

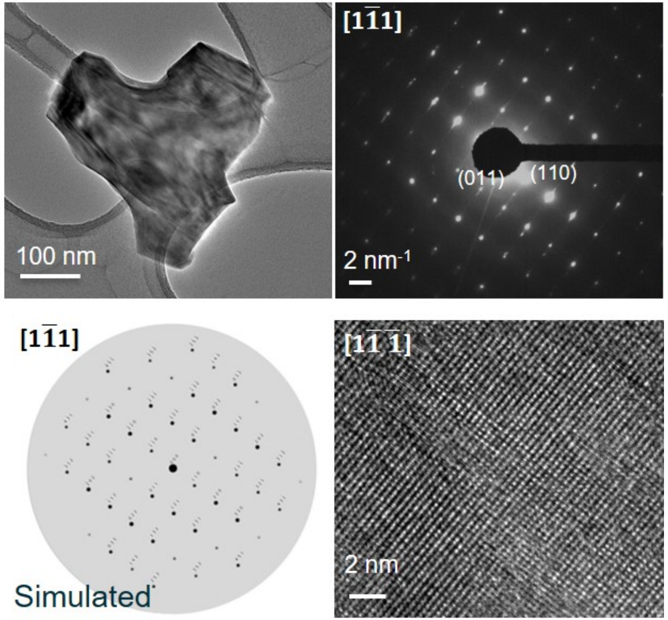
Synchrotron X-ray diffraction



Raman spectroscopy



High-resolution transmission electron microscopy

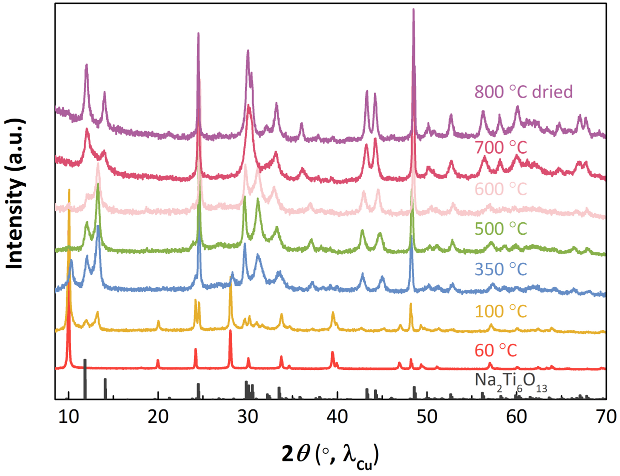


- The body-centered orthorhombic symmetry is largely maintained after Cs^+/Na^+ ion exchange.
- Increase of interlayer distance despite the smaller Na^+ ion size compared to Cs^+, suggesting hydration of Na^+.

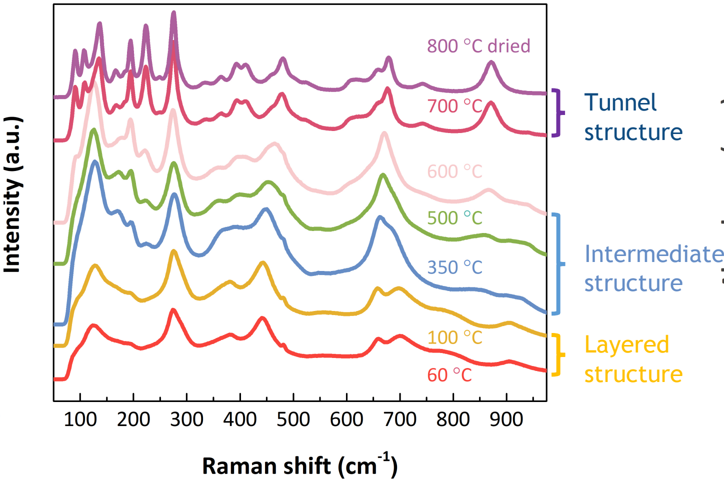
Technical Accomplishments

Thermal behavior of lepidocrocite-structured titanate $Na_xTi_{2-x/4}\square_{x/4}O_4$; x=0.74

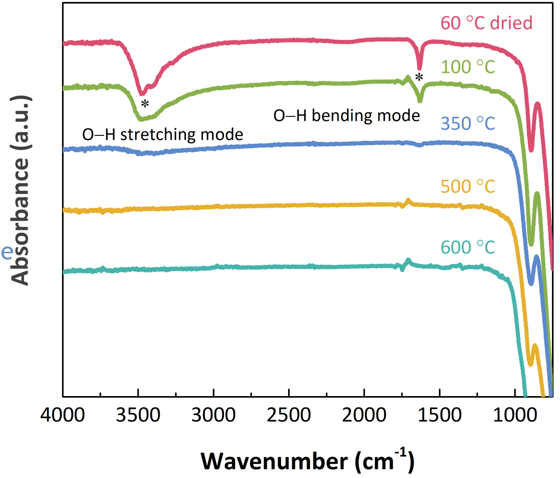
Laboratory X-ray diffraction



Raman spectroscopy



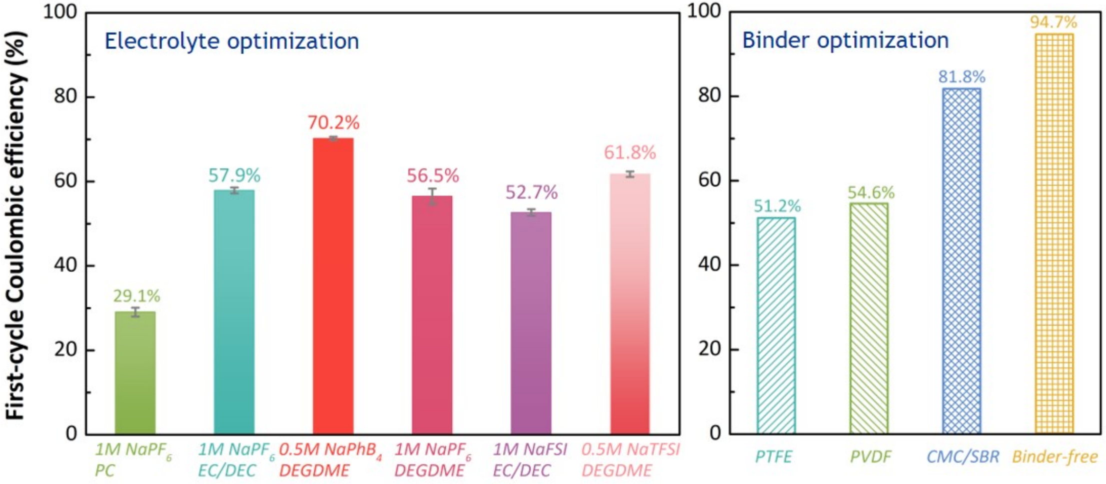
Fourier transform infrared – Attenuated total reflection

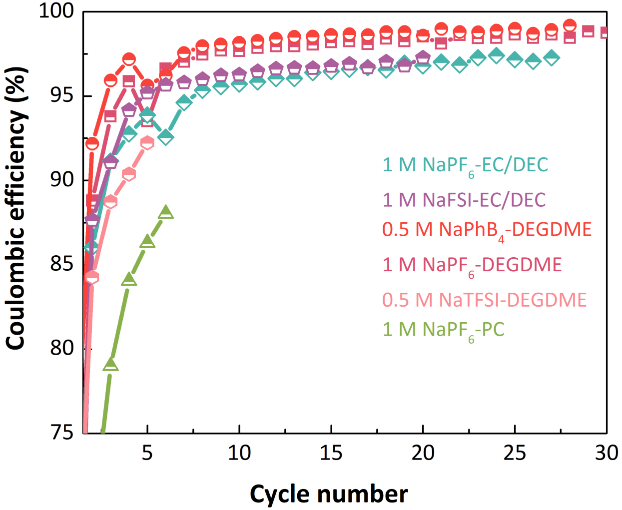


- Layered to tunnel structure transition occurs upon heating the material.
- Lepidocrocite-structured titanate is hygroscopic, the presence of physiosorbed water is observed.

Technical Accomplishments

Improving coulombic efficiency - electrolyte and binder optimization



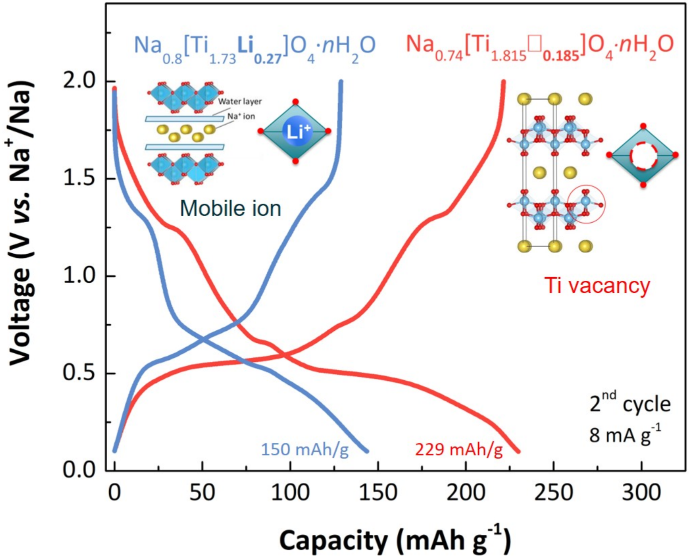


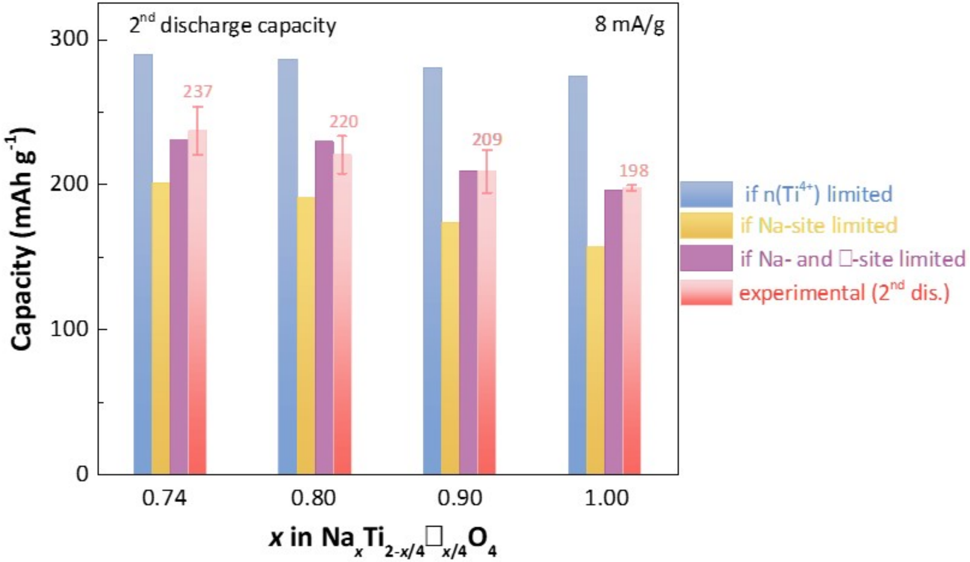
- 0.5M $NaPhB_4$ in DEGDME, showing the highest coulombic efficiency, is selected as the best electrolyte.
- High initial coulombic efficiency of 81.8 % and 94.7 % are obtained, respectively, for titanate electrodes using CMC/SBR binder and without binder.

Technical Accomplishments

Electrochemical characterization of $Na_xTi_{2-x/4}\square_{x/4}O_4$; x=0.74 - Na^+ storage capacity

Sodium half cell, second electrochemical cycle





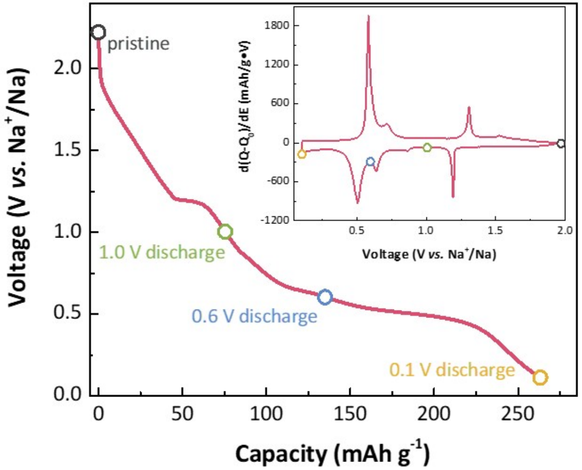
- Beneficial role of having Ti vacancies: increased capacity, decreased Na^+ storage voltage.

- Capacity of titanates is limited by the number of available sites for accommodating Na^+.
- The achievable capacity is higher than the theoretical capacity of titanates if considering only the interlayer sites.

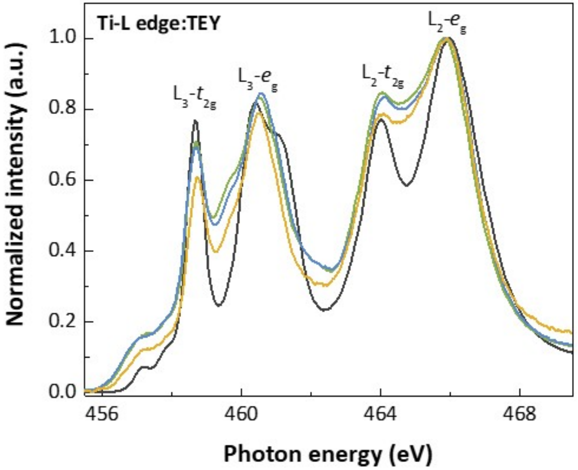
Technical Accomplishments

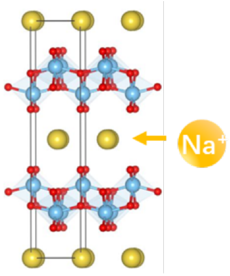
Na^+ storage mechanism of $Na_xTi_{2-x/4}\square_{x/4}O_4$; $x=0.74$

Preparation of ex-situ samples

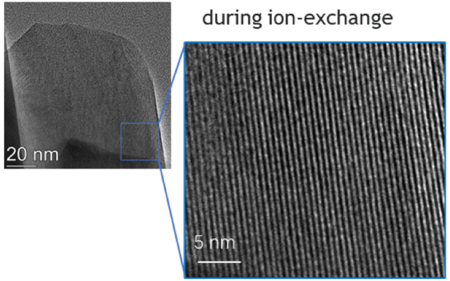


Soft X-ray absorption spectroscopy





Reductive Na^+ intercalation into interlayer sites



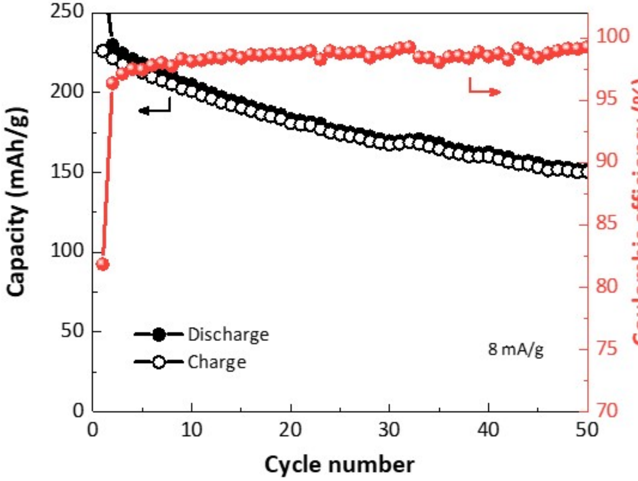
surface exfoliation during ion-exchange

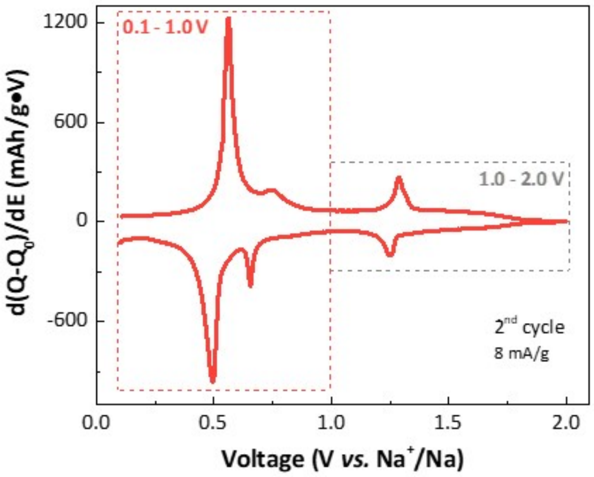
Na^+ storage into surface defect sites

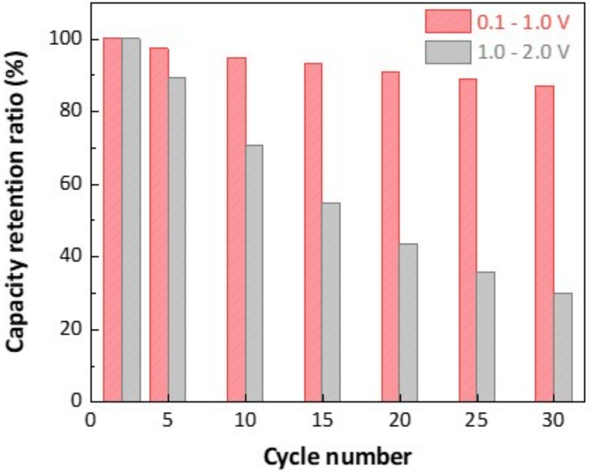
- Surface Ti reduction is evident, broader e_g peak suggests distortion of TiO_6 octahedra.
- Change of bulk Ti oxidation state will be probed by hard X-ray absorption spectroscopy on May 16, 2021.

Technical Accomplishments

Electrochemical characterization of $Na_xTi_{2-x/4}\square_{x/4}O_4$;x=0.74- capacity retention



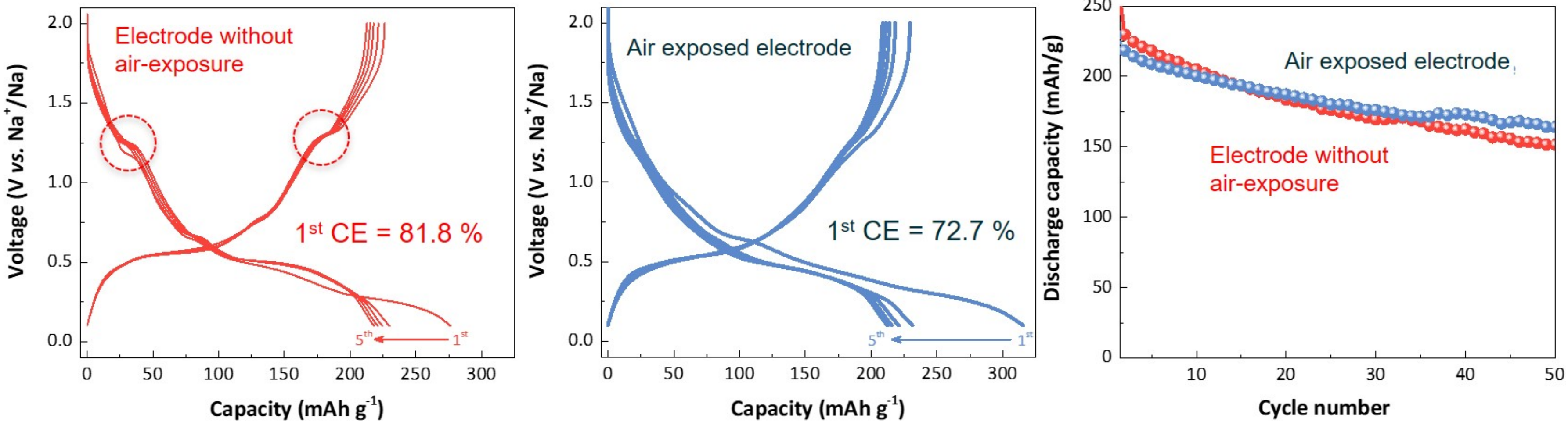




- 66 % of the 2nd discharge capacity at 50th cycle.
- Capacity fades more rapidly in high-voltage (1.0 – 2.0 V) than in low-voltage (0.1 – 1.0 V) region.

Technical Accomplishments

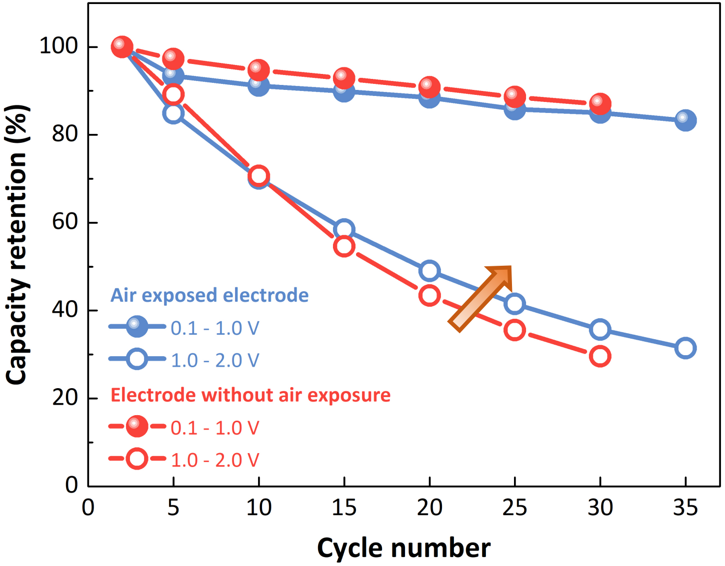
Electrochemical characterization of $Na_xTi_{2-x/4}\square_{x/4}O_4;x=0.74$ - sensitivity to air-exposure

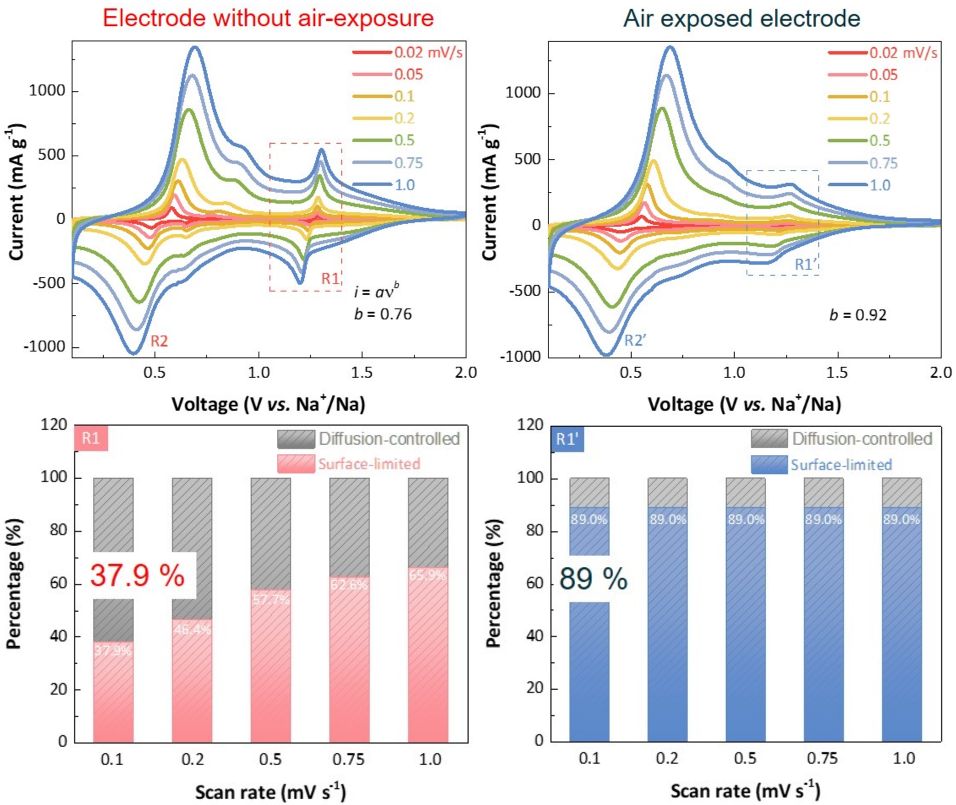


- Exposing titanate electrode to air for short period of time (ca. 10 min) slightly decreases the initial coulombic efficiency, modifies the voltage profile, and somewhat surprisingly, improves the capacity retention.

Technical Accomplishments

Electrochemical characterization of $Na_xTi_{2-x/4}\square_{x/4}O_4;x=0.74$ - sensitivity to air-exposure



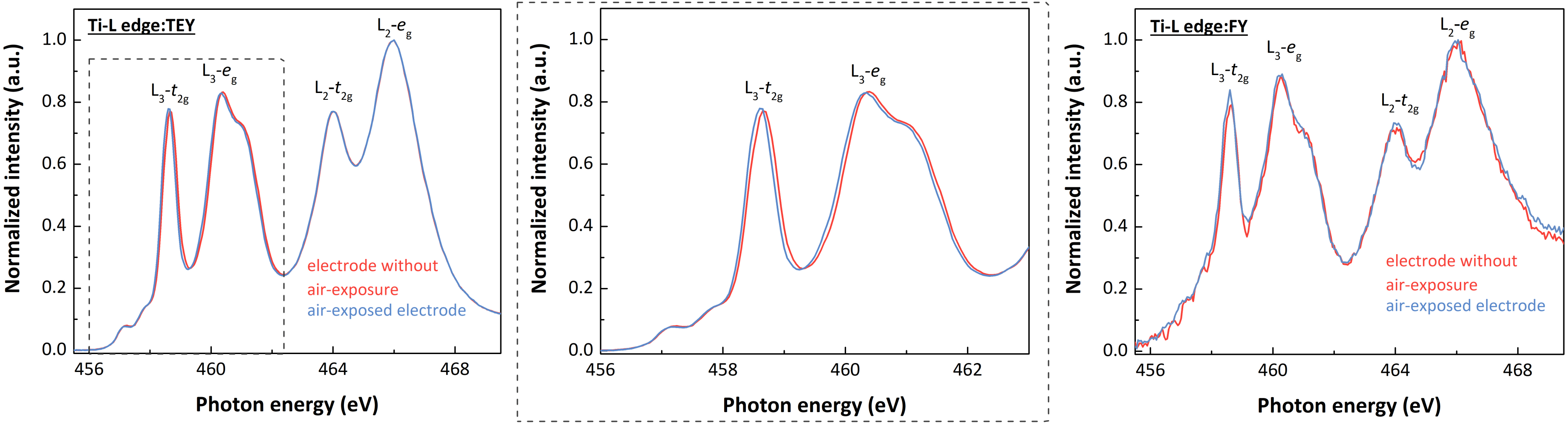


- Air exposure improves the capacity retention in the high-voltage region (1.0 - 2.0 V) by increasing the capacity contribution of a more reversible surface Na^+ storage reaction.

Technical Accomplishments

Change of $Na_xTi_{2-x/4}\square_{x/4}O_4;x=0.74$ electrode after air-exposure

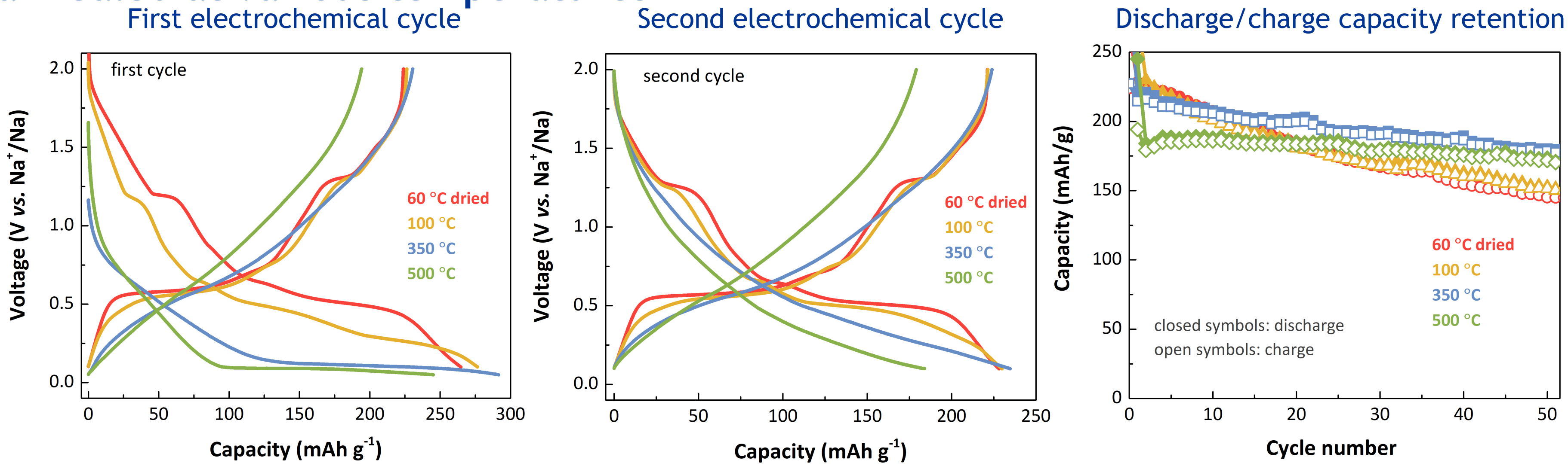
Soft X-ray absorption spectroscopy



- In the near surface region (5 – 10 nm, TEY mode), Ti L_3 edge position slightly shifts to lower energy after air-exposure.
- In the bulk of the material (100 nm, FY mode), Ti L edge spectra remain unaltered.

Technical Accomplishments

Electrochemical properties of $Na_xTi_{2-x/4}\square_{x/4}O_4$; x=0.74 annealed at various temperatures



First electrochemical cycle

Second electrochemical cycle

Discharge/charge capacity retention

- Heat treatment modifies the voltage profile, decreases the Na^+ storage voltage, and improves the capacity retention.
- 500 °C heat-treated material delivers 94.3 % of the 2nd discharge capacity at 50th cycle, whereas 66 % is achieved for 60 °C heat-treated sample.

Response to Previous Year Reviewers’ Comment

Not Available

Collaborations

Collaborators	Role
Dennis Nordlund, Apurva Mehta, SSRL	Synchrotron XAS and XRD studies

Remaining challenges and barriers

- ☐ The electrochemical properties of lepidocrocite-type titanate and sodium nonatitanate electrodes at the full-cell level should be evaluated. This will require some cell optimization.

- ☐ The change of bulk Ti oxidation state of titanate electrodes upon cycling will be studied using hard X-ray absorption spectroscopy.

- ☐ Due to the pandemic, there was limited access to synchrotron facilities, so some experiments and milestones had to be postponed. However, we will be able to complete the needed experiments by the end of the project.

Proposed Future Work

- Probe change of bulk Ti oxidation state of titanate electrodes using hard X-ray absorption spectroscopy.
- Test the electrochemical properties of lepidocrocite-type titanate and nonatitanate electrodes at the full-cell level.
- Our follow-on project will focus on the effects of vacancies, defects, and heat treatments on the electrochemical properties of stepped layered titanates, with a specific goal of improving cycle life. More characterization in full cells is planned

"Any proposed future work is subject to changes based on funding levels."

Summary

- ☐ The structure and surface properties of lepidocrocite-structured titanate were characterized using synchrotron XRD, Raman, FTIR-ATR and HR-TEM.
- ☐ The structure evolution upon heating lepidocrocite-structured titanate was studied, and the electrochemical properties of heat-treated samples were evaluated: heat treatment improves the capacity retention (94.3% and 66% of the 2^{nd} discharge capacity at 50th cycle were obtained respectively for 500°C- and 60°C heated sample).
- ☐ The electrolyte and binder are optimized to improve the coulombic efficiency: 0.5M $NaPhB_4$/DEGDME and CMC/SBR binder are the optimized combination.
- ☐ Based on electrochemical analysis, HR-TEM, and soft XAS results, the Na^+ storage mechanism of lepidocrocite-structured titanate is determined to be both reductive intercalation into interlayer sites and Na^+ storage into surface active sites, with possible Na^+ storage into Ti vacancy sites.
- ☐ The capacity of lepidocrocite titanate fades more rapidly in the high-voltage (1.0 – 2.0 V) region than in the low-voltage region (0.1 – 1.0 V vs. Na^+/Na), due to the less reversible Na^+ storage into surface-active sites which primarily occurs in high-voltage region.
- ☐ The electrochemical properties of lepidocrocite titanate is strongly affected by its surface properties: short-term electrode air-exposure modifies its electrochemistry (voltage profile, initial coulombic efficiency, capacity retention).