Titanium Niobium Oxide-Based Lithium-Ion Batteries for Extreme Fast-Charging Applications

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THE UNIVERSITY OF TENNESSEE KNOXVILLE

BIG ORANGE. BIG IDEAS.

Project ID: bat397

June 12, 2019

OAK RIDGE National Laboratory

Overview

Timeline

- Task Start: 7/1/18
- Task End: 6/30/20
- Percent Complete: 40%

Budget

- Total task funding
  - $720k
- $360k in FY19
- $360k in FY20

Barriers

- Barriers Addressed
  - Existing chemistries need improvement in extremely fast charge (XFC) and energy density.
  - Abuse Tolerance.
  - Achieve deep discharge cycling of 1000 cycles for EVs by 2022.

Partners

- Collaboration: ORNL
- Project Lead: University of Tennessee

Relevance & Objectives

- Relevance: Lithiation potential of graphite is very low that lithium plating cannot be avoided under extremely fast charge condition, leading to safety issues.
- Main Objective: Develop TNO based anode materials with high electronic conductivity and high capacity for extremely fast charging applications with a target energy density of 180 Wh/kg.
- Objectives in this period

➢ Enhance the electronic conductivity and lithium diffusion coefficient of TNO by self-doping.

➢ Enhance the electronic conductivity of TNO by surface coating with carbon.

Project Milestones

Date	Milestones and Go/No-Go Decisions	Status
Nov. 30, 2018	Milestone Finish evaluation of self-doped TNO.	Complete
Jan. 31, 2019	Milestone Finish electrolyte formulation to improve the coulombic efficiency and cycle stability of NMC based half cells.	Complete
April 30, 2019	Milestone Finish full cell optimization of the TNO based full cells using coin cells.	On tract
June 30, 2019	Go/No-Go Decisions Determine whether increasing surface area can improve rate capability but not decrease the coulombic efficiency.	On tract
July 31, 2019	Milestone Fabricate and deliver nine 2Ah pouch cells to DOE.	On tract

Project Approach

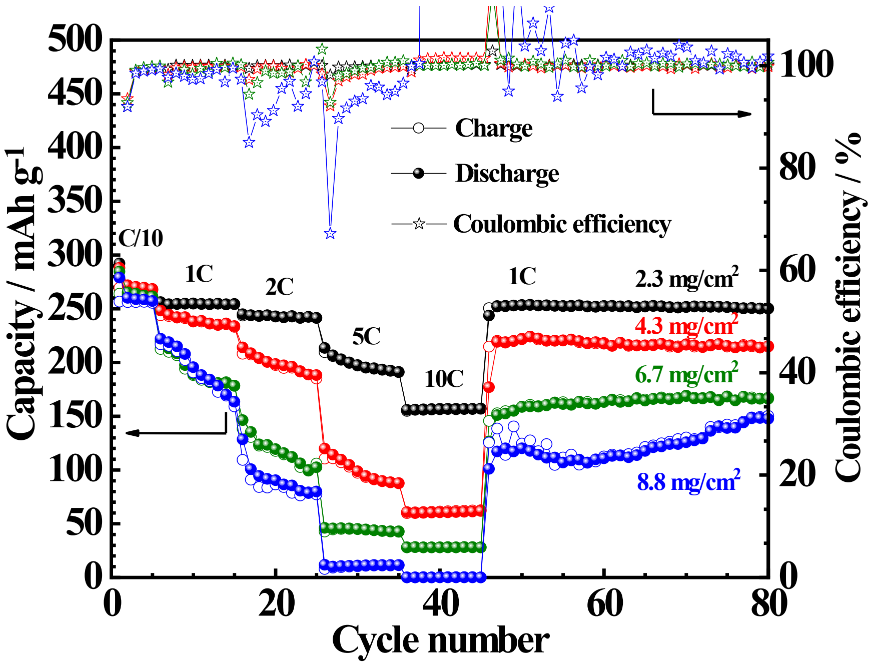
- Problems:
  - Electronic conductivity of TNO is low.
  - Achieved capacity is much lower than theoretical capacity.
  - Low energy density in the cells with extremely fast charging.

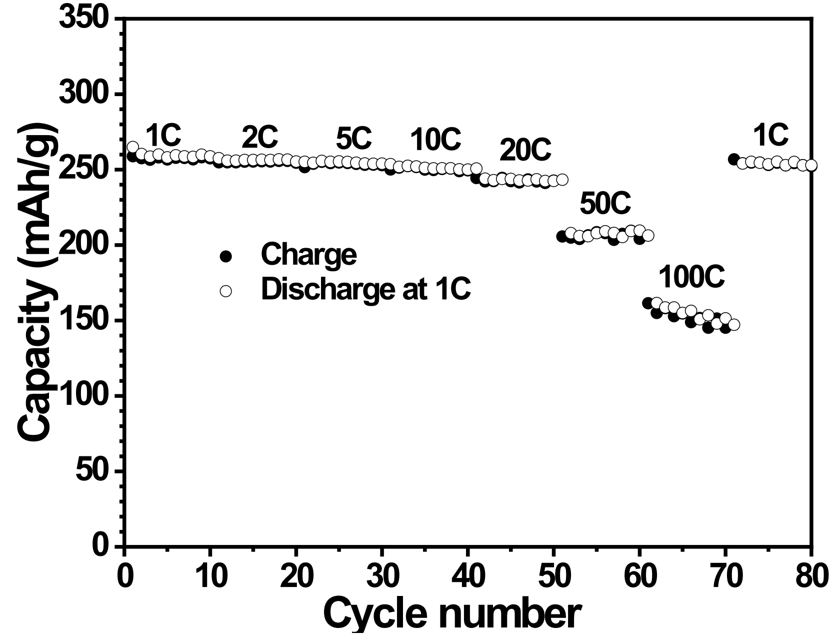
- Technical approach and strategy:
  - ➢ Enhance rate capability by formation of porous structure.
  - ➢ Improve electronic conductivity by doping and surface coating with carbon.
  - ➢ Synthesize large scale TNO with low cost precursors.
  - ➢ Evaluate rate performance and long term cyclability of coin cells with high loading TNO.
  - ➢ Improve long term cyclability of coin full cells using functional additives.
  - ➢ Evaluate rate performance and long term cyclability of pouch full cells.

Technical Accomplishments- Executive Summary

- Synthesized porous $TiNb_2O_7$ (TNO) with low-cost niobium chloride, achieving similar performance as previously reported.
- Evaluated the effect of active material loading on high rate performance of TNO half-cells.
- Synthesized carbon coated porous TNO material (TNO@C) with low-cost glucose and facile hydrothermal approach.
- Demonstrated that 1 wt% carbon coating maintained the TNO's structure intact and delivered the best rate performance and the highest initial coulombic efficiency.
- Evaluated high rate performance of high loading NMC622 half-cells.
- Confirmed that active material loading was the critical factor for the full-cell performance with a 10 min charging protocol.
- Demonstrated the best cycling stability of full cells at a high charge rate of 4C.
- Achieved higher capacities of full-cells with a NMC622:TNO@C ratio of 1:1.

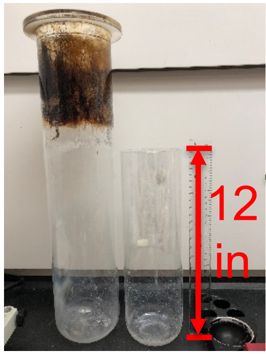
Technical Accomplishments - Investigated the loading effect on rate performance of TNO based half-cells





- $TiNb_2O_7$ (TNO) with porous structure was successfully synthesized with low-cost niobium chloride, achieving similar performance as previously reported for low loading of active material (right figure).
- High rate performance decreases dramatically with increasing TNO loadings.
- Low electronic conductivity of TNO material is the bottleneck for high rate performance.

Technical Accomplishments - Synthesized carbon coated TNO



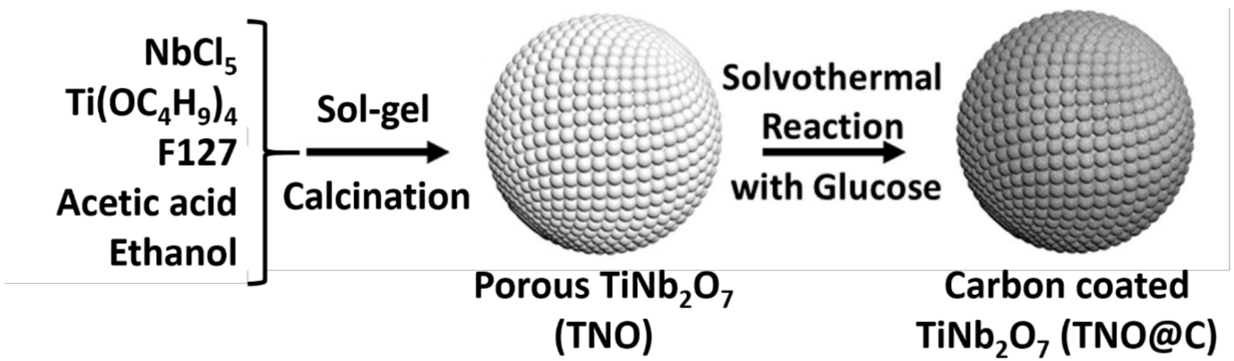
Inner crucible

Calcinating furnace

Sieve shaker

Hydrothermal autoclave

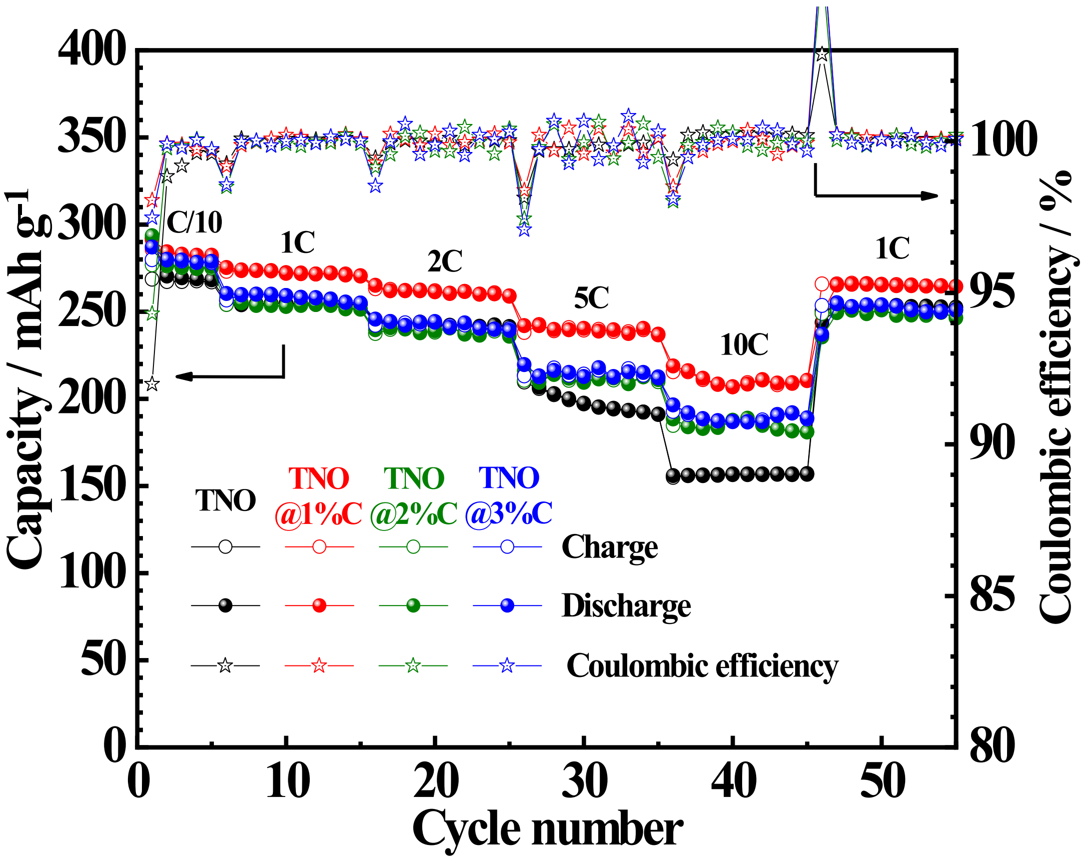
Tube furnace



Synthetic procedure for carbon-coated porous $TiNb_2O_7$ (TNO@C) particles

- Low-cost glucose was used as the carbon source to coat porous TNO (TNO@C) via a hydrothermal approach.

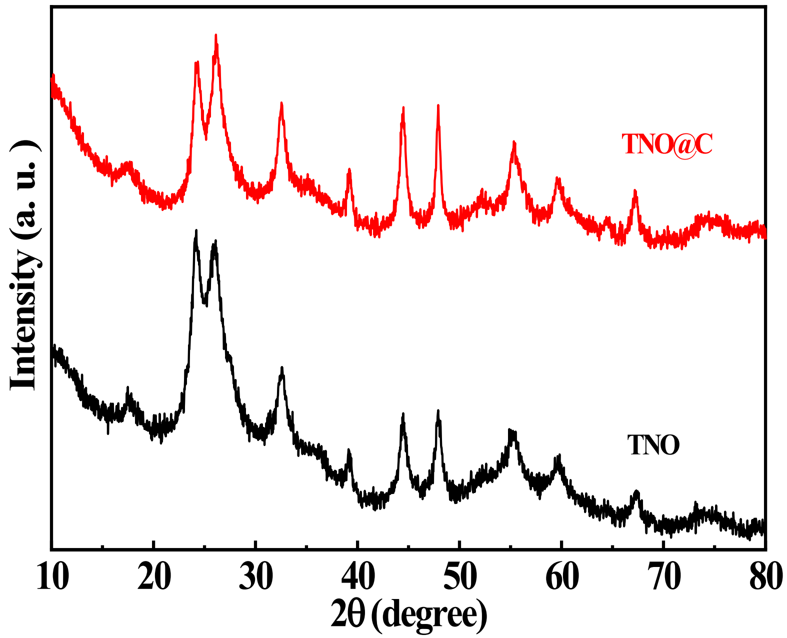
Technical Accomplishments - Investigated the effect of carbon coating on rate performance

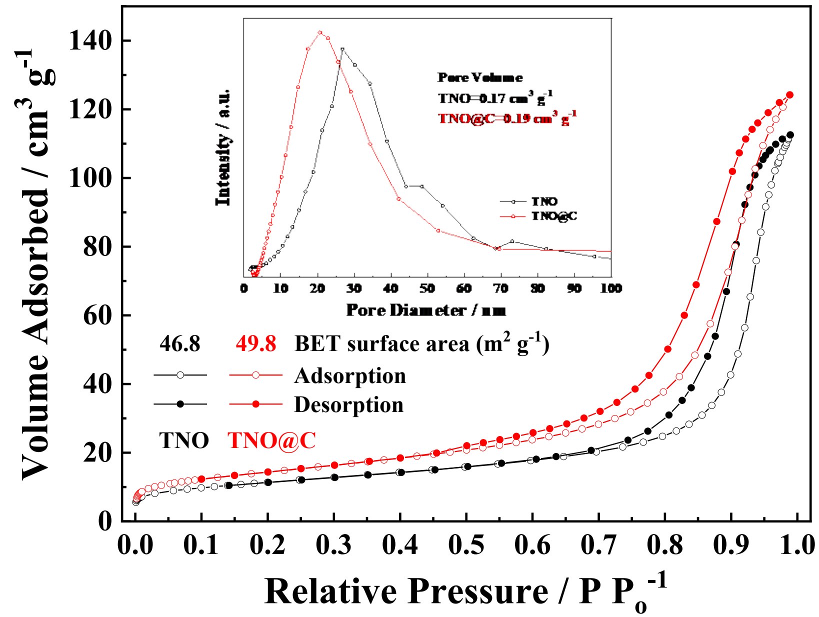


Rate performance and coulombic efficiencies of pristine and carbon coated TNO based half-cells (the TNO loading is 2.3 mg cm^{-2}).

- The amount of carbon coating can be easily controlled by the ratio of TNO and glucose precursor.
- TNO@C with 1 wt.% carbon coating delivers the best rate performance and increases the initial coulombic efficiency to 98%, as compared to 92% of pristine TNO.

Technical Accomplishments - The consistent structure of TNO@C

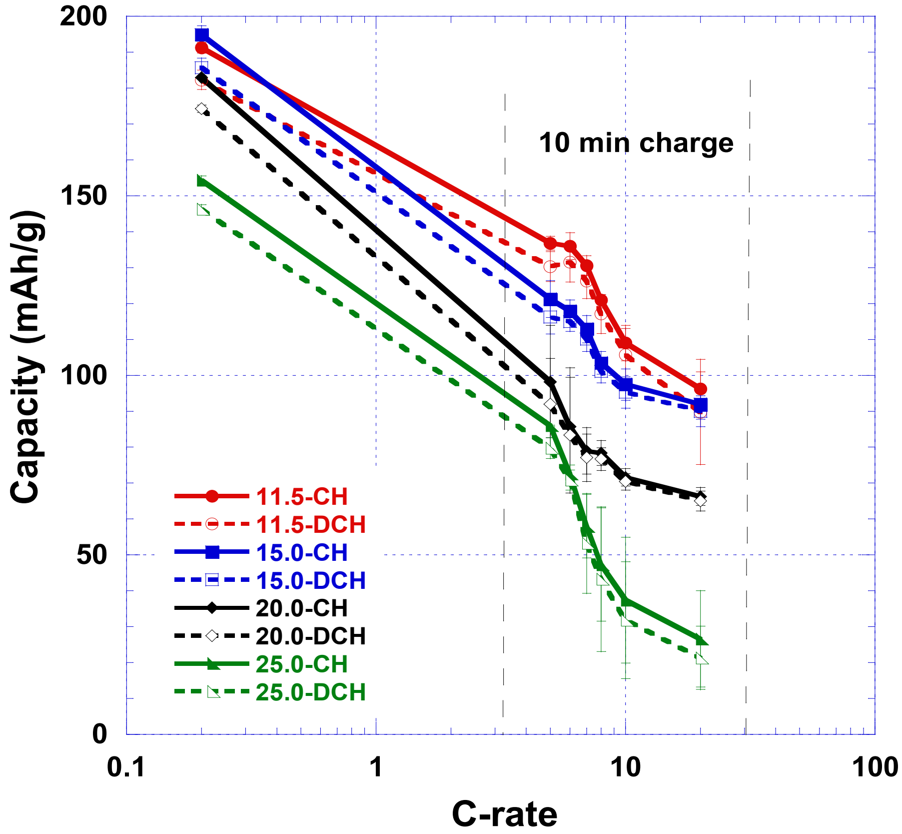




XRD (left) and BET (right) of as-prepared TNO and TNO@C materials

➢ Surface carbon coating does not affect the structure, surface area and pore size distribution of TNO.

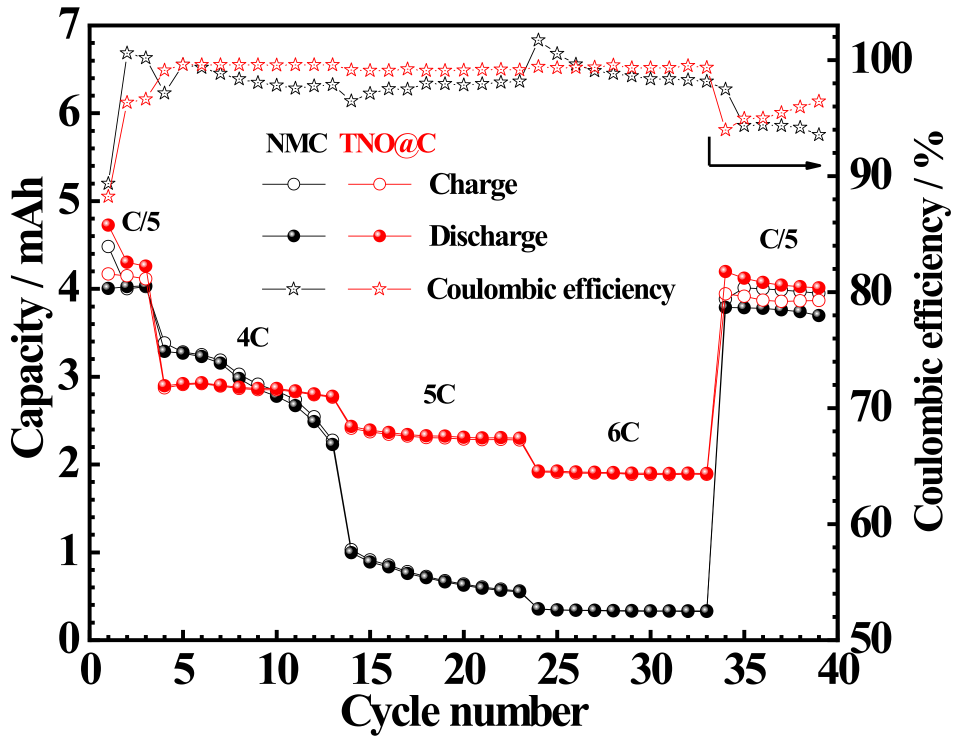
Technical Accomplishments - Evaluation of NMC622 half cells with different loadings and charge protocols



- Test protocol: 5 cycles of charge/discharge at C/5 (1C = 175 mA/g), followed by 10 min total charge with different constant current and constant voltage (CCCV) protols. The discharge rate is C/3.
- The fast charge capacity decreases dramatically with increasing areal loading.
- The highest loading of 25 mg/cm^2 has only < 55% capacity retention at 10 min charge.

Rate performance of NMC622 half coin cells with different areal loadings (11.5-25.0 mg/cm^2) at various charge protocols.

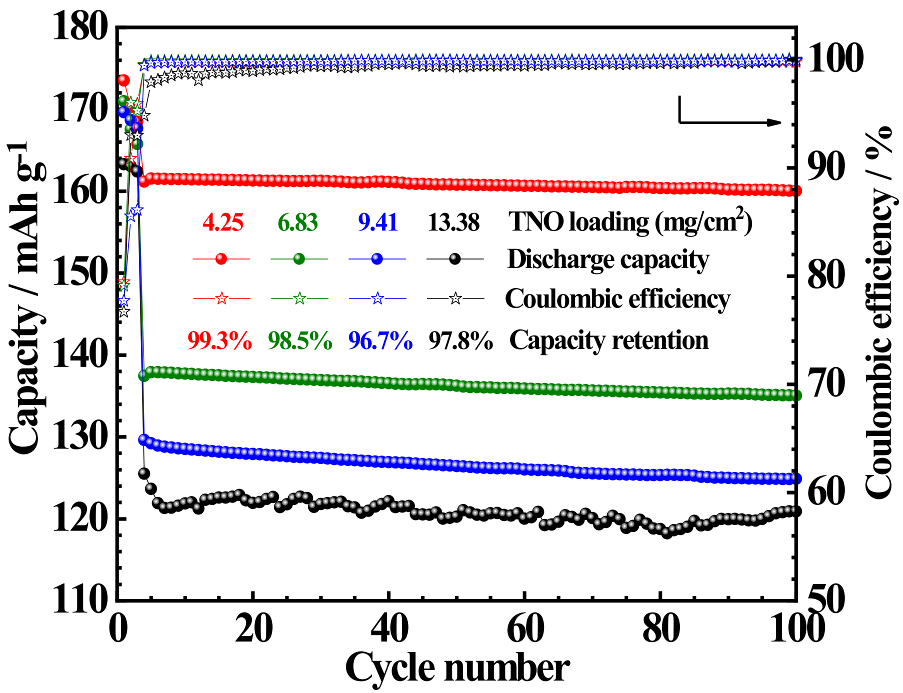
Technical Accomplishments - Evaluation of high-loading half-cells under high rates

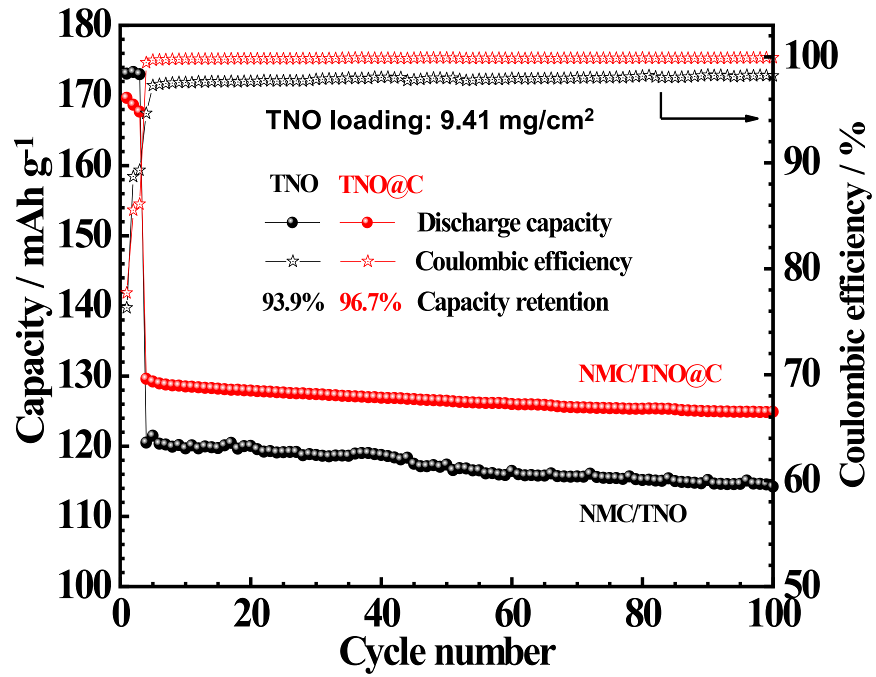


High rate performance and coulombic efficiencies of NMC622 and TNO@C half-cells (18 and 13.5 mg/cm^2 for NMC622 and TNO@C, respectively).

- Protocol: Three initial cycles at a rate of C/5 (1C=150 mA/g for NMC622 and 200 mA/g for TNO@C).
- For NMC622, charge rates changed while the discharge rate was fixed at C/3; For TNO@C, discharge current rates changed while the charge rate was fixed at C/3.
- The cathode is limiting in the current loadings.

Technical Accomplishments - Evaluation of full-cells with different matched electrode loadings



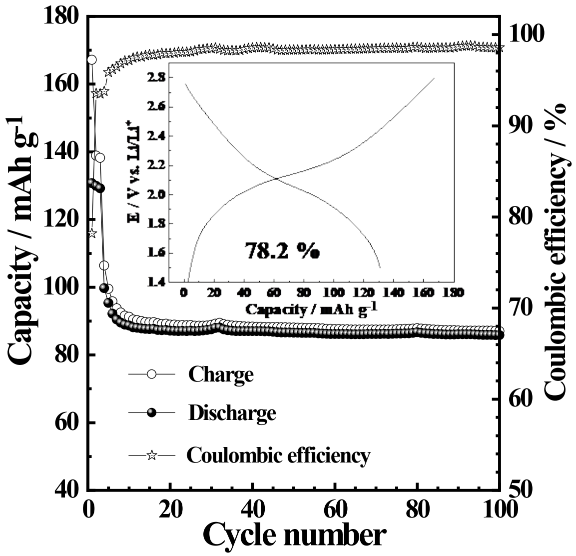


The full-cells with 1:1 active material ratio of NMC622 and TNO@C.

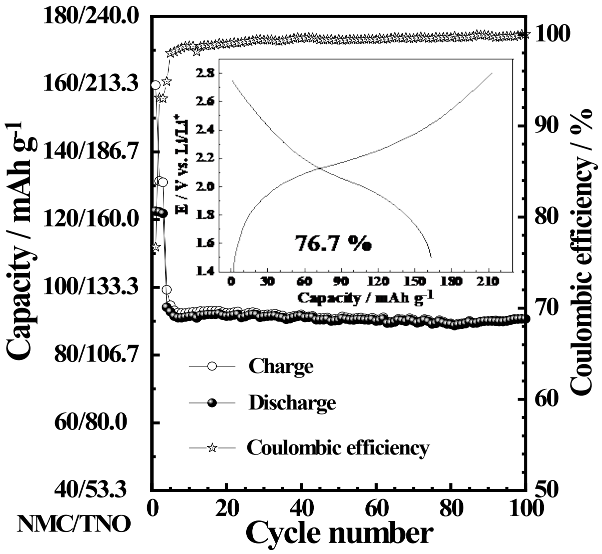
- Protocol: The cell was charged at 5C to 2.8 V and maintained at 2.8 V until the total 10 min charge time was reached and discharged at C/3.
- The loading of active material dramatically influenced the performance of the full-cells.
- The carbon coated TNO full cell delivered higher capacity than the uncoated one.

Technical Accomplishments - Investigated the effect of different active material ratios

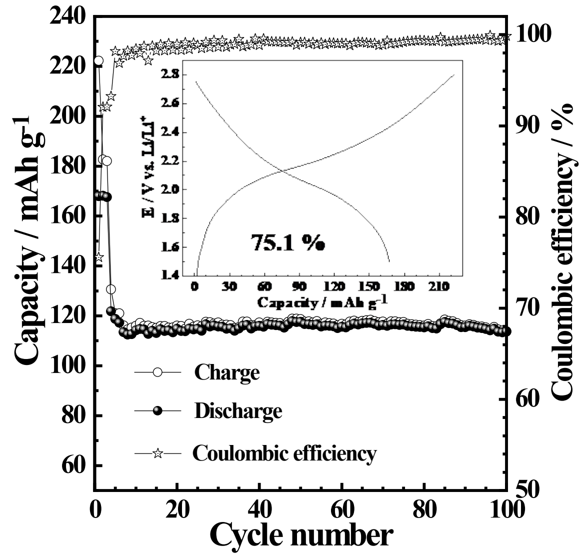
NMC622:TNO@C=1:1.1



NMC622:TNO@C=1:1



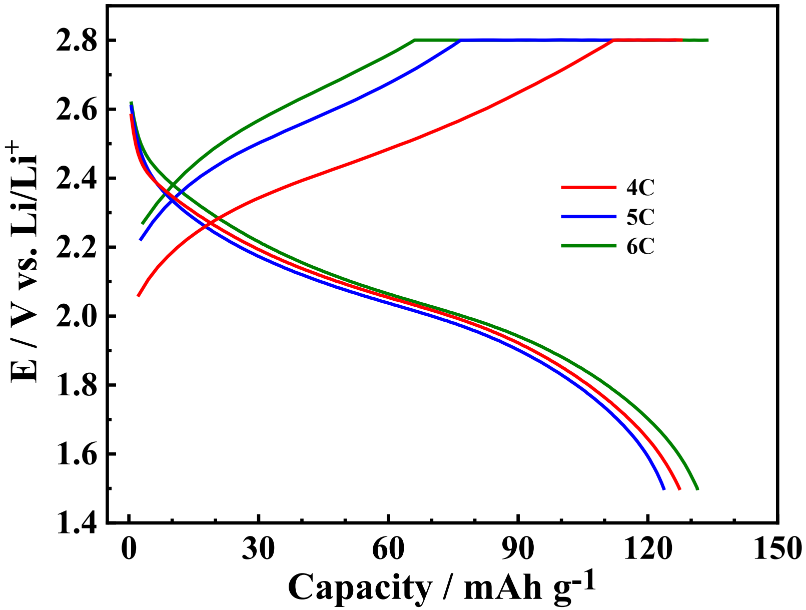
NMC622:TNO@C=1.1:1

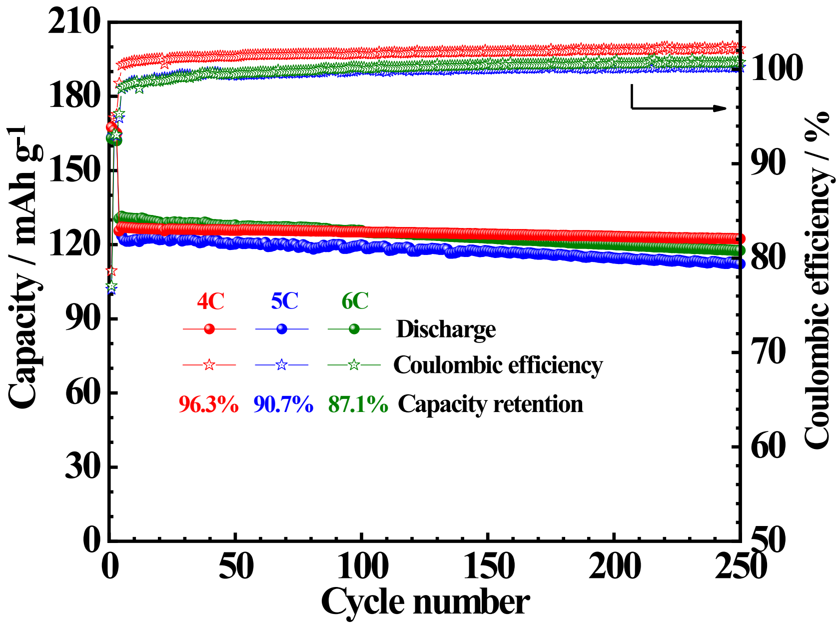


Cycling performance of full cells with different ratios of active materials with a total 10 min charge time at 5C and 2.8 V constant voltage.

- Higher amount of TNO@C resulted in higher initial coulombic efficiency.
- The full-cell with a NMC622:TNO@C ratio of 1:1 exhibited higher capacity.

Technical Accomplishments - Investigated the effect of different charge protocols on full cells





Cycling performance of NMC622/TNO@C full cells (three repeats) under different charge protocols with a total time of 10 min and discharge at C/3. (NMC622: ~18 mg/cm^2; TNO@C: ~13.5 mg/cm^2)

The charge protocol with a 4C charge (600 mA/g for NMC622 and 800 mA/g for TNO@C) delivered the best cycling stability with the smallest voltage polarization.

Collaborations

Partners

- National Labs: Oak Ridge National Laboratory
- Active Material Suppliers: TODA America, ConocoPhillips
- Inactive Material Suppliers: Solvay Specialty Polymers, Ashland

Future Work

Remainder of FY19

- Fabricate NMC and TNO based pouch cells.
- Optimize cycling protocol to increase capacity and improve cycling stability.
- Fabricate and deliver nine 2Ah pouch cells to DOE.

FY20

- Large scale synthesis of transition metal doped TNO.
- Surface coating transition metal doped TNO with carbon.
- Synthesize and evaluate lithium malonatoborate salts as additives.
- Fabricate and optimize transition metal doped TNO full cells with coin cells.
- Fabricate and evaluate transition metal doped TNO pouch cells.
- Fabricate and deliver eighteen 2Ah pouch cells to DOE.

Summary

Objective:

- Develop TNO based anode materials with high electronic conductivity and high capacity for extremely fast charging applications with a target energy density of 180 Wh/kg.

Approach:

- Enhance rate capability by formation of porous structure.
- Improve electronic conductivity by surface coating with carbon.
- Synthesize large scale TNO with low cost alternative precursors.
- Evaluate rate performance and long term cyclability of coin cells with high loading TNO.
- Improve long term cyclability of coin full cells by using functional additives.
- Evaluate rate performance and long term cyclability of pouch full cells.

Technical:

- Synthesized porous $TiNb_2O_7$ (TNO) with low-cost niobium chloride, achieving similar performance as previously reported.
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- Evaluated high rate performance of high loading NMC622 based half-cells.
- Confirmed that active material loading was the critical factor for the full-cell performance under a 10 min charging protocol.
- Demonstrated the best cycling stability of full cells at a high charge rate of 4C.
- Achieved higher capacities of full-cells with a NMC622:TNO@C ratio of 1:1.

Acknowledgements

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