



## Extreme fast charging characteristics of zirconia modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode for lithium ion batteries



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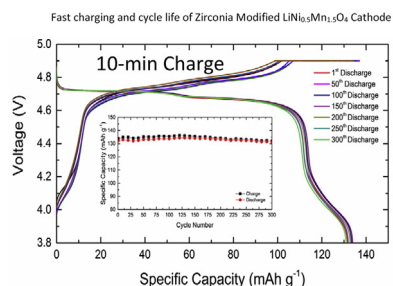
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### HIGHLIGHTS

- $\text{ZrO}_2$ - $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  withstands 80C-rate and demonstrates over thousand cycles at 40C.
- Charge transfer resistance at  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /electrolyte is stable with coating.
- Origin of high-rate capability is correlated with the high kinetics at the material's interfaces.
- Surface modification of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  enables extreme fast charging.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

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### ABSTRACT

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  is a promising high-voltage cathode for lithium-ion battery fast charging applications. Aware of its electrochemical stability issues, the material's surface is modified with small amounts of zirconia ( $\text{ZrO}_2$ ) ranging from 0.5 to 2 wt% using a scalable ball milling process. The advantage of the coating has been demonstrated in electrochemical measurements performed at room temperature and 55 °C, and in cells discharged under high-rate conditions up to 80C. Of significance, the material coated with 1.0 wt%  $\text{ZrO}_2$  has been cycled at the 40C rate for over a thousand cycles and retains 86% of its initial capacity. The material with 2.0 wt%  $\text{ZrO}_2$  modification preserves 76% of its initial capacity when cycled at the 40C rate and 55 °C. The coated materials have shown excellent cycling stability when subjected to 6C (10-min) fast charging and C/3 discharging for 300 cycles. Compared to the uncoated material, the interfacial resistance of the zirconia modified  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  has been found to be much lower and does not significantly increase with increasing the coating amount. However, the electrochemical performances are still partly limited by both interfacial resistance at the beginning of charge and electrolyte diffusivity, particularly under higher rate cycling conditions. Overall, the strategy of  $\text{ZrO}_2$  surface modification applied to  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  unveils the potential that the material could play in extreme fast charged electric vehicles.

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## 1. Introduction

The fast-growing markets for consumer electronics, electric vehicles and renewable energies are increasingly catalyzing the development of advanced battery systems that are suitable in terms of energy and power densities, safety, cost and performance for the various energy applications [1,2]. Due to high-voltage and -energy density advantages, lithium-ion batteries have dominated the portable electronics market since last two decades, and are making steady strides towards the electrification of personal and public transportation [3–5]. Currently, lithium ion batteries have completely captured the portable electronics market, and the goal is now directed towards more penetration in electric vehicles (EVs) [3,6,7]. Yet, the available Li-ion battery technology still suffer from safety and energy density weaknesses, and in particular, from the fast charging shortcoming that may not catalyze the wide acceptance of electric vehicles.

At the materials level, the spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (labeled LNMO) is a very promising cathode due to its high energy density resulting from the product of its high-operating voltage (4.7 V vs. Li) and theoretical capacity ( $147 \text{ mAh}\cdot\text{g}^{-1}$ ). However, the unsatisfactory cycling performance must be addressed prior to enabling the material in commercial lithium-ion batteries. Indeed, the coupling of the oxidation of electrolytes and parasitic reactions during the high-voltage operation of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  leads to rapid capacity fade, especially at elevated temperature where manganese dissolution further degrades the cycle life [8–12]. Recently published review reports discussed details regarding the merit and major shortcomings of the material [13,14]. To mitigate these issues, several research approaches had been adopted including the doping for Mn/Ni [15–20], particles size and morphology tailoring [21–24], structural disorder and lithium concentration tuning [25,26], and surface modification [27–30]. The latter involved the use of various coating materials such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{MgO}$ , and  $\text{ZnO}$  in order to reduce the undesirable interfacial side reactions, and hence improve the cycle life of LNMO [27,30–34]. Recently published reports on  $\text{ZrO}_2$  as a coating material showed good performance of this material [35,36]. The caveat is that most of these surface modification approaches used complex chemical processes with difficulties in controlling the uniformity and thickness of these coatings [37–39]. In many instances, the interfacial resistance, which originates from the coating, can rather hinder the rate capability of the material.

Instead, any reliable coating approach on battery materials should be first cost effective and scalable despite any performance improvements. Second, there are still substantial uncertainties on how these coatings work in enhancing the electrochemical performance [25,28–32]. Indeed, it appears that nano-sized thin coatings can help in providing some improvements in battery cycle and calendar lives; however, thick coatings may act as a migration barrier for lithium transport resulting in capacity and rate performance decays [37,40]. Consequently, a quantitative study is needed to unveil the trade-off between the interfacial transport/kinetics (capacity and rate capability) and interfacial protection (cycle life) in a given battery coating strategy.

In this study,  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  has been coated with zirconia ( $\text{ZrO}_2$ ) nano-size particles. Unlike most coating processes, the method involved the use of a soft and scalable ball milling technique in which increasing amounts of  $\text{ZrO}_2$  (0.5–2 wt%) were introduced to  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  just before the final calcination. The obtained materials have been characterized by x-ray diffraction (XRD), scanning and transmission electron microscopies (SEM and TEM), and electrochemical charge and discharge. We also used the electrochemical impedance spectroscopy (EIS) to characterize the electrode/electrolyte interfaces before and after coatings. This process has resulted in significantly improving the life of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  under high-temperature ( $55^\circ\text{C}$ ) and high-rate performance (10-min charge) conditions. Our observation is that the material with 1.0 wt%  $\text{ZrO}_2$  coating exhibited better rate performance at ambient temperature, while that with 2.0 wt%  $\text{ZrO}_2$  coating showed better life span at  $55^\circ\text{C}$ . The overall results demonstrated that the

adopted  $\text{ZrO}_2$ -coating method could pave the way in enabling  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  as an advanced cathode material for extreme fast charging and long-cycle life lithium-ion battery applications.

## 2. Experimental

### 2.1. Materials preparation

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (LNMO) was prepared via sol-gel using lithium, nickel and manganese acetates (Sigma Aldrich) in the molar ratio 1.05:0.5:1.5, respectively. The precursors were dissolved in distilled water in the presence of citric acid. The molar ratio total-ions/citric-acid was 2:1. Ammonia was added to the transition metals solution dropwise until the pH of the solution reached 8. The resulting solution was kept at  $70^\circ\text{C}$  until a transparent gel was obtained. The gel was dried in an oven at  $100^\circ\text{C}$ , and then decomposed at  $450^\circ\text{C}$  for 6 h in air before final calcination at  $900^\circ\text{C}$  for 12 h. The surface modified LNMO was synthesized by addition of  $\text{ZrO}_2$  nano-powder (Sigma Aldrich,  $< 100 \text{ nm}$  (TEM)) to the material that was treated at  $450^\circ\text{C}$ , and ball milling for 24 h using zirconia balls media. In this case, the nominal weight percentages of  $\text{ZrO}_2$  in the composite were 0.5, 1.0, 1.5, 2.0 wt%. After ball milling, the composites  $\text{ZrO}_2$ -LNMO were calcined at  $900^\circ\text{C}$  for 12 h in air. The heating and cooling rates were set at  $5^\circ\text{C}/\text{min}$ .

### 2.2. Physical characterization

Powder-XRD (Rigaku) using Cu-K $\alpha$  radiations was used to identify the phase purity of the synthesized materials. The particle morphology was investigated by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800). The material surface was investigated with X-ray photoelectron spectroscopy (XPS) (Thermo-Scientific-Sigma Probe).

### 2.3. Electrode fabrication

The positive electrodes were fabricated by casting slurries composed of 75 wt% LNMO active material or  $\text{ZrO}_2$ -LNMO, 17 wt% conductive carbon (Super-P) and 8 wt% poly (vinylidene fluoride) binder in 1-methyl-2-pyrrolidone (NMP) on an aluminum foil using doctor blade. The electrodes were dried at  $80^\circ\text{C}$  to remove NMP, and then vacuum-dried at  $120^\circ\text{C}$  to remove traces of moisture. The electrodes were cut into several disks of 12 mm diameter and  $25 \mu\text{m}$  thickness. The active material loading was  $\sim 1 \text{ mg}/\text{cm}^2$  for all the measured cells.

### 2.4. Electrochemical measurements

Electrochemical measurements were carried out using 2032-type coin cells assembled with bare-LNMO or  $\text{ZrO}_2$ -LNMO in an Ar-filled glove box. Lithium foil was used as the negative electrode. The electrolyte was made of 1 M  $\text{LiPF}_6$  dissolved in a solvent mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by v/v.). Galvanostatic charge/discharge tests were performed at 25 and  $55^\circ\text{C}$  using Solartron battery cyclers (1470 E). The cells were tested under fast-charge and slow-discharge rate conditions and vice-versa to check the rate performance of the materials. To ensure reproducibility of results, several cells were subjected to the same testing conditions.

### 2.5. GITT and EIS measurements

The cells were initially charged and discharged using a current density equivalent to the C/10 rate to form stable solid electrolyte interphases (SEI) at both the positive and negative electrode interfaces. During a typical experiment, the C/10-equivalent current was applied at the start of the charge for 1 h to reach a certain state of charge, and then a 3-h rest was applied to reach the steady-state cell voltage. This procedure was repeated stepwise to cover all states of charge and

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