



## Simultaneously fabricating homogeneous nanostructured ionic and electronic pathways for layered lithium-rich oxides

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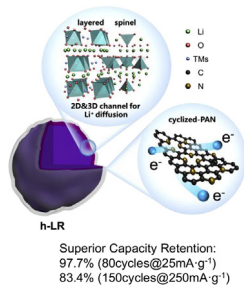
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### HIGHLIGHTS

- Ionic and electronic pathways were fabricated outside the  $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$  (LMNO).
- LMNO with bicontinuous pathways shows improved cycling and rate performances.
- The formation mechanism of the ionic and electronic pathways are discussed.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Layered Li-rich oxides (LLROs) have been considered as promising cathodes for next-generation Li-ion batteries due to their low cost and high reversible capacity. However, drawbacks such as voltage decay and poor cycle & rate performance hinder their commercialization. These problems are mainly related to the interface reaction and herein we fabricate nanostructured ionic and electronic bicontinuous pathways for  $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$  simultaneously by modifying the cyclized-polyacrylonitrile (c-PAN) on the surface. This unique design constructs spinel structure on the surface of layered materials as the 3D pathway for Li-ions and conductive framework for electrons to transfer from the current collector through the acetylene black to the surface of every single particle as well, therefore providing both ionic and electronic pathways. Electrochemical tests shows that the cycle & rate performances of the material are significantly improved. After 80 cycles at 0.1C ( $1\text{C} = 250\text{ mA g}^{-1}$ ), the capacity retention reaches 97.7%. The results identify that the conductive modification is conducive to maintain the capacity from the spinel phase and control the amorphization of the material, thereby helping to get remarkable cycle performance. We also propose the mechanism of spinel phase formation. This bicontinuous pathways design opens up significant opportunities for the novel design of lithium-rich oxides.

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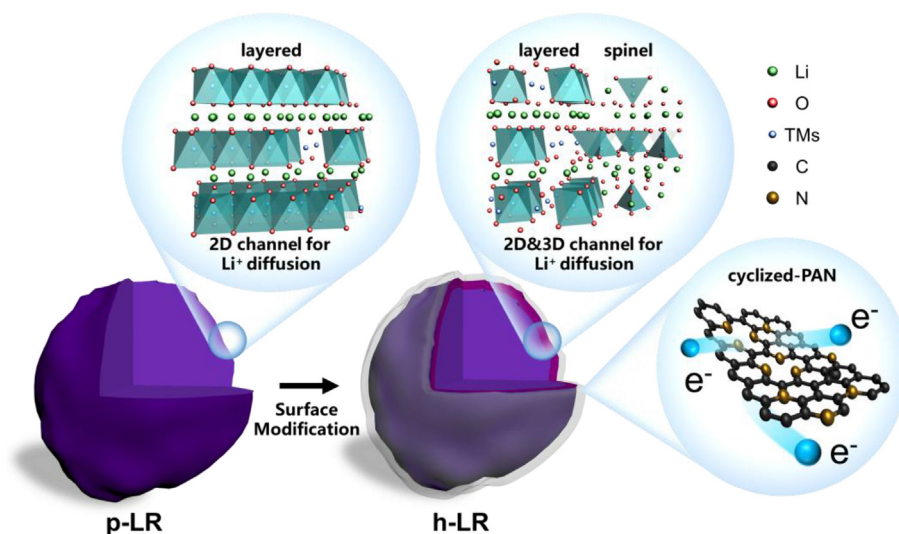


Fig. 1. Schematic diagram of as-prepared p-LR and h-LR material.

## 1. Introductions

The annual demand for the lithium-ion battery is rapidly growing over the world [1–3], however, the energy density of commercial lithium-ion batteries (LIBs) is insufficient to meet the demand of all-scale applications especially for electric vehicles (EVs) and hybrid electric vehicles (HEVs). The average range per charge is dissatisfactory when considering the practicability. In essence, the energy density of LIBs depends on the capacity of cathode and anode materials and their potential differences. Since the traditional anode materials graphite is gradually replaced by silicon/carbon composite and the specific capacity is toward  $600 \text{ mAh}\cdot\text{g}^{-1}$ , while the capacity of the cathode is still  $\sim 200 \text{ mAh}\cdot\text{g}^{-1}$  ( $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Al}_{0.1}\text{O}_2$ ) [4] or less and the progress is mired [5,6]. The major method for improving the energy density of LIBs is to find alternative high-capacity cathodes.

The development of layered lithium-rich oxides (LLROs) has brought hope since their specific capacity is over  $250 \text{ mAh}\cdot\text{g}^{-1}$ , coupled with intrinsic advantages such as low-cost and low-toxicity [7–9]. This class of compounds is usually written as  $x\text{Li}_2\text{MnO}_3(1-x)\text{LiMO}_2$  ( $M = \text{Ni}, \text{Mn}, \text{Co}, \text{etc.}, 0.5 \leq x < 1.0$ ) in which lithium ions occupy both lithium layers and part of transition metal (TM) layers in a close-packed oxygen framework [10]. The unique arrangement brings a high specific capacity to LLROs since  $\text{Li}^+$  in the TM layers can be distracted at 4.5 V or above with oxygen in the first cycle, thus activating the insulating  $\text{Li}_2\text{MnO}_3$  component [11–13]. Nevertheless, this activation process is irreversible, leading to low initial coulombic efficiency. Another severer problem is that LLROs suffer from obvious voltage decay during long cycling [14,15], which is caused by the travel of partial transitional metal ions from their own layer to lithium layer during the high cut-off voltage cycling. Cycle & rate performances of LLROs are also discouraging, because of the poor delithiation kinetics in the Mn-related process (mostly in the  $\text{Li}_2\text{MnO}_3$  component) [16]. These drawbacks hinder the commercialization of LLROs seriously.

So far, various strategies have been deployed to improve LLROs, such as structural design, coating and doping [17–26]. Namely, both electrons and Li-ions pathways should be continuous to achieve the intrinsic capacity of the electrode. The mismatch of active particles with the conductive agent hinders the full performance of active material and even deteriorate the stability [27–29]. As for electronic pathways, the disparate particle sizes of active materials ( $\sim 10 \mu\text{m}$ ) and acetylene black ( $\sim 30 \text{ nm}$ ) in conventional electrodes are compatible since acetylene black can easily distribute around active material particles, however, nano-sized active particles encounter the severe aggregation due to high interface energy, thus it is challenging to disperse them

with acetylene black uniformly. As for ions pathways, recent research found that layered/spinel hetero-structure would be an optimized choice for Li-rich oxides since the existence of 3D  $\text{Li}^+$  diffusion pathways in spinel phase, which is also effective to suppress oxygen activity. Hence, several approaches have been utilized to obtain the hetero-structure lithium-rich materials with preeminent electrochemical performance [30–35]. However, the homogeneous distribution of spinel structure coating/embedding nano-sized particles of LLROs is challenging until now, let alone simultaneously fabricating rapid ion and electron transport pathways.

It has been found that PAN can cyclize at the limited pyrolysis temperature (e.g.  $\sim 300^\circ\text{C}$ ) in the inert atmosphere to generate delocalized  $\text{sp}^2 \pi$  bonding for intrinsic electronic conductivity, while the polymeric properties can be retained due to the intermolecular cross-linking and conjugation [36–39]. Hence, cyclized-polyacrylonitrile (c-PAN) that can homogeneously coat on the electrode materials due to its ductility was applied here, combined with traditional acetylene black, to provide continuous electron transport pathways for every single particle. In addition, this cyclization process accompanies a slight dehydrogenation reaction that can be used for creating oxygen vacancies on the surface of the lithium-rich material, building partial spinel structure to provide 3D  $\text{Li}^+$  transport pathways [40]. Naturally, benefit from the homogeneous distribution of c-PAN, this approach realized uniform coating of spinel structure, and thus establishing bicontinuous transport pathways for nano-sized  $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$  particles. The schematic figure of this design is illustrated in Fig. 1. This unique bicontinuous design contributes greatly to the cycle and rate performance of  $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ . Moreover, the mechanisms of spinel formation and remarkable capacity retention are discussed as well.

## 2. Experiment

### 2.1. Synthesis & preparation

The LLRO material with a chemical formula of  $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$  was synthesized by a facile Sol-Gel method [41,42]. To modify pristine  $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$  (labelled as p-LR) particles, polyacrylonitrile (J&K Corporation, average M.W. = 150000) with 5 wt% to the pristine  $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$  was first dissolved in the N,N-Dimethylformamide (DMF), the mass ratio of solute and solvent was adjusted to 1:100 and then the solution was stirred thoroughly until all PAN dissolved. The pristine  $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$  powder was then added in followed by 3 h ultrasonic treatment. The mixture was stirred vigorously at  $60^\circ\text{C}$  until the solution evaporated, and the as-prepared material was heated at

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