



On the functionality of the polypyrrole nanostructures for surface modification of Co-free Li-rich layered oxide cathode applied in lithium-ion batteries



Parisa Vahdatkhal^{a,b}, Sayed Khatiboleslam Sadrnezhad^{a,*}, Oleksandr Voznyy^{b,*}

^a Department of Materials Science and Engineering, Sharif University of Technology, 11365-9466, Tehran, Iran

^b Department of Physical & Environmental Sciences, University of Toronto, Toronto, ON M1C 1A4, Canada

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ABSTRACT

Co-free Li-rich manganese nickel oxide (LMNO) materials are emerging as an up-and-coming candidate for high-energy-density cathodes. However, they suffer from severe cycling capacity fading and poor performance rates. Herein, the surface functionalization of an LMNO cathode is designed by polypyrrole (PPy) nanostructure coating. We found that PPy nanoparticles@LMNO cathode exhibits high-capacity retention and enhanced rate capabilities, delivering a discharge capacity as high as 191 mAh g⁻¹, with capacity retention of 96%, after ~ 200 cycles at a current density of 20 mA g⁻¹. The results indicate that the intercalation and doping pseudocapacitance can be varied depending on the synthesis process, morphology (nanowire/nanorod/nanoparticle), size, dispersity, and weight percentage of PPy. Our findings provide an effective strategy to improve the ionic and electronic conductivity of LMNO cathodes and demonstrate that high-capacity and long cycle-life Li-ion batteries can be achieved by regulating the contribution of the intercalation and doping pseudocapacitive charge storage behavior.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) with high energy densities are considered the primary power source for portable equipment and next-generation electrified transportation [1]. The Co-free Li-rich manganese nickel oxides (γ -Li₂MnO₃(1-y)LiNi_{1-x}Mn_xO₂, LMNO) have attracted considerable interest because of their high specific capacity as high as 250 mAh g⁻¹ due to the reversible anion and cation redox reactions [2–3]. Despite their ability to provide significantly high capacity, several performance limitations include poor rate capability, poor cyclic stability, and low initial coulombic efficiency [4].

The progressive structural rearrangements associated with irreversible transition-metal migration, the phase transition from layered to spinel structure, and oxygen release are the major causes of LMNO's capacity fade and structural instability, which are reported that originate from the surface [5–6]. Besides, the oxidation of alkyl carbonate-based electrolytes occurs at high working voltages of LMNO (> 4.5 V) [7]. Therefore, different surface modifications with metal oxides [8–11], fluorides [12], and phosphates [13] have been developed to overcome the problems mentioned above. Nevertheless, the complexity of continuous coating and damage the bulk material after the other

heat-treatment process on the surface of LMNO, which is required to crystallize the coating, exist in most inorganic coating materials. Furthermore, the low electronic/ionic conductivity of inorganic materials resulted in the poor rate capability of cathode [7].

Among the conductive polymers foreseen to resolve such issues, polypyrrole (PPy) hold great promise due to its unique intrinsic properties such as high electrical conductivity, easy synthesis procedure, environmental stability, and good redox behavior [14]. Numerous studies have been devoted to developing the electrochemical performance of some anodes and cathodes of the LIBs with PPy [7,15–16,34,24–33,17–23]. PPy presents pseudocapacitive charge storage property via the mechanism of reversible electrochemical doping [35]. It has been reported that the PPy possesses a theoretical capacity of 72 mAh g⁻¹ in the range of 2.0–4.5 V vs. Li/Li⁺ as a host structure for Li-ion [36]. It is worth noting that PPy nanostructures exhibit outstanding electrochemical and electrical behavior [37]. Thus, understanding the impact of the chemistry of PPy nanostructures on their pseudocapacitive properties could effectively streamline the energy storage applications of PPy-modified materials. However, the surface modification of Co-free LMNO with different kinds of PPy nanostructures has not been fully revealed so far.

* Corresponding authors.

E-mail addresses: sadrnezh@sharif.edu (S. Khatiboleslam Sadrnezhad), o.voznny@utoronto.ca (O. Voznyy).