



# Surface modification of $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ nanoparticles with polydopamine-assisted $\text{MgF}_2$ coating



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## ABSTRACT

Nano-sized  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  powder is vulnerable to reaction with the electrolyte because it has a wide electrolyte/cathode contact area. In order to avoid this, we modified the surface of the nano-sized  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  powder by coating it with  $\text{MgF}_2$ . A polydopamine pre-coating layer served as a binding agent for the homogeneous  $\text{MgF}_2$  coating on the surface of the  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  nanoparticles. Polydopamine-assisted coating with  $\text{MgF}_2$  improved the discharge capacity, cyclic performance and thermal stability of the  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  cathode, possibly by suppressing side reactions between the electrolyte and the cathode.

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## 1. Introduction

Li-rich layered oxides are a promising new cathode material because of their extraordinarily large discharge capacity of over 200 mAh/g [1–5]. However, before these materials can be commercialized for high-energy LIBs applications, issues that must be addressed include poor cyclic performance, rate capability, and large irreversible capacity in the 1st cycle [5–7]. One approach to overcome these limitations in Li-rich layered oxides is to reduce their particle size [8–10]. Nanoparticles reduce the diffusion distance in Li ions and provide a wider contact area with the electrolyte, improving the rate capability. However, the increased surface area of the nanoparticles also facilitates undesired reactions with the electrolyte, such as dissolution of transition metals, which lower the cyclic performance of the cell [11]. To overcome this problem, we tried modifying the surface of nano-sized cathode particles with stable fluoride ( $\text{MgF}_2$ ). Surface modification prevents unwanted reactions on the surface of the cathode and protects the cathode material from attack by HF present in the electrolyte [11–20]. However, it is very difficult to homogeneously coat the surface of the nano-sized particles. Moreover, if the nano-sized cathode particles are not spherical, but are rather composed of various shapes, then the differences in

surface energies of the pristine particles hindered the homogeneous dispersion of the coating particles. The polydopamine pre-coating layer introduced herein as a binding agent, helps apply the coating homogeneously on the surface of the nano-sized cathode particles. The polydopamine layer on the surface of the nanoparticle can be used to modify the surface of the cathode in order to create a reactive platform, thereby facilitating the reaction with the coating material [21–24].  $\text{MgF}_2$  was selected as coating material because Mn, an inexpensive element, has been used as a doping material to enhance the electrochemical properties of cathodes [25,26]. Moreover,  $\text{MgF}_2$  has already been used as a coating material of cathode to suppress the unwanted reaction with electrolyte [27]. The  $\text{MgF}_2$ -coated  $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  nanoparticles not only show good electrochemical properties but also have improved thermal stabilities.

## 2. Experimental

Nanoparticles of  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  were prepared as reported previously [20]. The polydopamine pre-coating layer was applied by mixing the pristine  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  powder into a dopamine solution containing Tris buffer (10 mM; pH 8.5) (Aldrich) and methanol (Aldrich, 99.9%) as cosolvents, ( $\text{CH}_3\text{OH}$ /buffer (1:1 (v/v))). The mixture was mechanically stirred at room temperature until all the particles were suspended in the solution. The mixture was then centrifuged, washed several times with ethanol and distilled water, and dried at 90 °C for 24 h. To produce the  $\text{MgF}_2$  coating solution, magnesium nitrate hexahydrate [ $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] and ammonium fluoride [ $\text{NH}_4\text{F}$ , Aldrich] were

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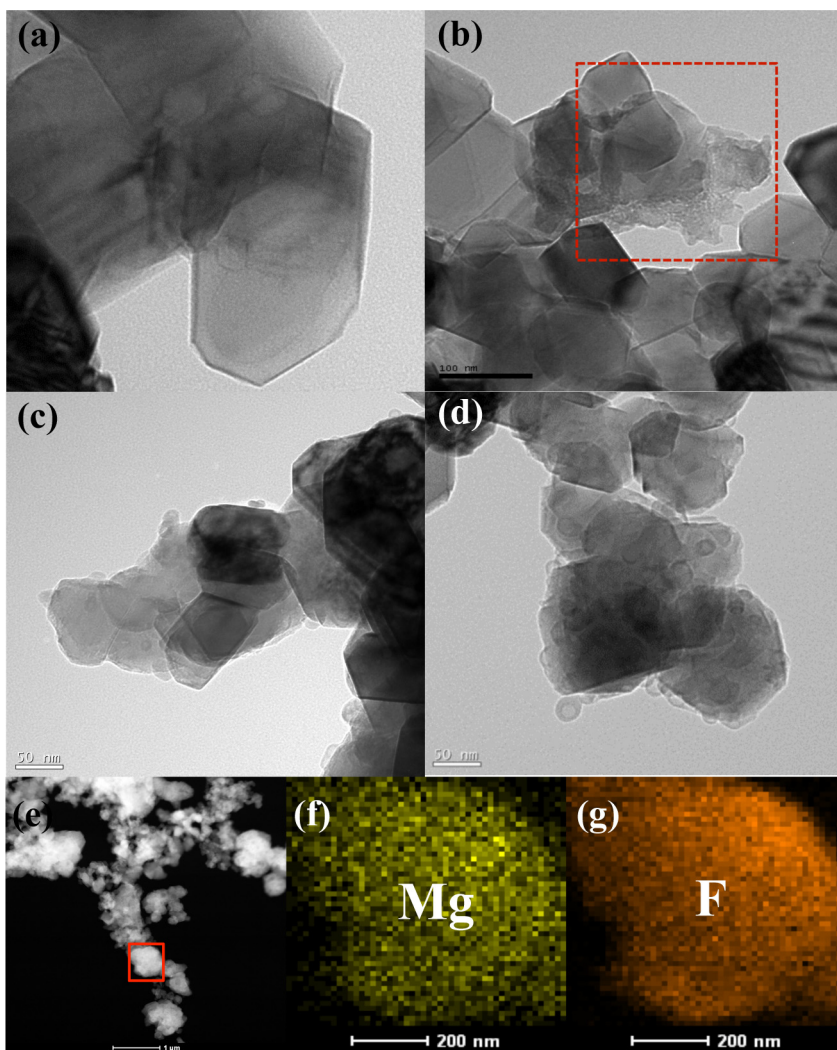
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dissolved in ethanol. The polydopamine-coated powder was added to the  $\text{MgF}_2$  solution and stirred at  $50^\circ\text{C}$  until all the ethanol had evaporated. The sample was then dried at  $90^\circ\text{C}$  for 24 h and annealed at  $400^\circ\text{C}$  for 4 h in air. Annealing the sample removes the polydopamine pre-coating layer present on the surface of the powder.

The surface morphology of the samples was observed using a transmission electron microscope (TEM) (AP tech TECNAI G2 F30 S-Twin) operating at 200 kV. For electrochemical testing, a slurry was prepared by mixing cathode powder, carbon black (Super P) and polyvinylidene fluoride (PVDF) in a weight ratio of 80:12:8. A coin-type cell (2032) comprising a cathode, a Li-metal anode, a separator and an electrolyte was used. The electrolyte was 1 M  $\text{LiPF}_6$  dissolved in a mixture of ethylene carbonate/dimethyl carbonate (EC/DMC) in a 50:50 volume ratio. The cells were subjected to galvanostatic cycling using a WonATech voltammetry system. Thermal stability of the fully charged electrode (4.8 V) was analyzed by differential scanning calorimetry (DSC) (Mettler Toledo). Two milligrams of the positive electrode-containing electrolyte was sealed in a high-pressure DSC pan. The heating rate and temperature range in the DSC tests were  $5^\circ\text{C}/\text{min}$  and  $25\text{--}300^\circ\text{C}$ , respectively.

### 3. Results and discussion

The surface morphology of the pristine and  $\text{MgF}_2$ -coated  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  nanoparticles was observed by TEM. As shown in Fig. 1a, the pristine particles were 100–500 nm in size and had various shapes. Surface coatings have previously been applied to spherical cathode particles several micrometer in size [11–19]. Spherical particles have homogenous surface energy, which promotes the homogeneous attachment of the coating particles onto their surface. Differences in the surface energy of non-spherical cathode powders prevent the coating particles from achieving a homogeneous dispersion on the surface of the cathode powders. Pristine particles of a smaller size are also less likely to exhibit homogenous attachment of coating particles on their surface. Fig. 1b is a TEM image of the  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  nanoparticles coated with  $\text{MgF}_2$  by a typical wetting process, which consists of mixing the pristine powder with a solution containing the Mg and F source materials without the polydopamine pre-coating layer. As expected, the coating particles are not dispersed on the surface of the cathode particles but are instead mostly aggregated as shown by the red square. This indicates that without the polydopamine pre-coating, the  $\text{MgF}_2$  coating layer was



**Fig. 1.** TEM images of the  $\text{Li}[\text{Ni}_{0.2}\text{Li}_{0.2}\text{Mn}_{0.6}]\text{O}_2$  powder. (a) Pristine (uncoated) sample. (b)  $\text{MgF}_2$ -coated sample prepared without using a polydopamine pre-coating layer. (c) Sample coated with 0.25 wt%  $\text{MgF}_2$  using a polydopamine pre-coating layer (d and e) Sample coated with 0.5 wt%  $\text{MgF}_2$  using a polydopamine pre-coating layer. The red square in (e) is the area that was analyzed by TEM-EDS. EDS maps of (f) Mg and (g) F. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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