Optimally designed interface of lithium rich layered oxides for lithium ion battery

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Abstract

Particle morphology structure design combined with surface modification has been applied to improve the **electrochemical properties** of lithium rich layered oxides. Hollow spherical lithium rich layered $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ oxides with different shell thickness are synthesized by co-precipitation followed by calcination. The morphology and interior structure have been investigated by SEM and cross section, and their electrochemical properties have been evaluated to identify an appropriate shell thickness. Furthermore, a **Zr compound** coating layer has been applied to modify the interface between corrosive electrolyte and hollow spherical particles with an appropriate shell thickness. The Electrochemical impedance spectroscopy shows hollow spherical structure and **Zr compound** coating layer both can modificate the electronic and ionic transmission capacities and inhibit their deterioration during charge-discharge process at the same time. The HRTEM tests indicate that hollow spherical structure and **Zr compound** coating layer can dramatically suppress Mn dissolution in electrolyte and make the crystal structure more stable during the electrode process. Therefore, a surface modification combine with the hollow spherical structure (with an appropriate shell thickness) can effectively enhance these electrochemical properties of lithium ion layered oxides.

Keywords: Lithium ion battery; Lithium rich layered oxide; Hollow spheres; Surface modification

1. Introduction

With the extensive application of lithium ion battery, more and more attentions are being paid on its performance especially the capacity. Present commercial cathode materials, such as LiCoO_2 / LiMn_2O_4 / $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ / LiFePO_4 , displays a specific capacity under 200 mAh g^{-1} , which is far below that of anode carbon materials.[1-3] Therefore, it is urgent to develop new cathode materials with larger capacity. In recent years, many researches concentrated on the lithium rich manganese layered oxides which delivered a discharge capacity range from 250 to 300 mAh g^{-1} . [4-9] However, the existence of electrochemical inactive Li_2MnO_3 results in the poor electron conductivity and low lithium ion diffusion coefficient, and then makes lithium rich manganese layered oxides show unsatisfactory rate capacity.[10, 11]

In the current study, elements doping, surface modification, and material nanocrystallization have been applied to improve the electrochemical properties of lithium rich manganese layered oxides.[12-16] Elements doping primarily used to enhance the crystal structure stability of materials during the electrode process, which can stabilize discharge plateau and achieving the stable energy density of the cathode, but has limited contribution to rate capacity. Carbon[17, 18] and graphene[19, 20] coating can facilitate both electronic and ionic conductivity leading to improve rate performance, but the effect on the corrosion resistance do not evaluated. Nanoparticles greatly shorten the lithium ion diffusion path and make particles contact with electrolyte well, but nanoparticle means large specific surface area, which could certainly destabilize materials in electrolyte, especially when the cut-off voltage is higher than 4.5 V.

Furthermore, it is more difficult to coat a protective layer on the surface of material since the particle size goes smaller and irregular, and then results in more exposed particle surfaces in corrosive electrolyte. [21]

Firstly, we propose an optimal designed hollow spherical structure for the lithium rich manganese layered oxide. The shell thickness of hollow spherical particles is range from 1.2 to 2.5 μm , which are tuned by controlling the architecture of precursor. Although the resistance for lithium ion diffusion grow with the thickness of shell, structure collapses of hollow spherical particles should be found easier to occur during powder processing when shell thickness declined to a certain value, which may lead to more surface area be exposed to electrolyte. Therefore, an appropriate shell thickness is necessary for hollow spherical materials to resist the corrosion from electrolyte, and own good electronic and ionic conductivity at the same time. Secondly, a high Li^+ diffusion coefficient **Zr compound** has been coated on the surface of hollow spherical $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ particles, which can further enhance the protection of hollow spherical $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ particles away from corrosive electrolyte. Obviously, this optimal design of particle surface can guarantee lithium rich manganese layered oxides a better electrochemical performance, which is significant in its development.

2. Experiment

The $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ sample is prepared by a solid state reaction from lithium carbonate and manganese-nickel-cobalt carbonate $\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}(\text{CO}_3)_{0.8}$. The precursor of $\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}(\text{CO}_3)_{0.8}$ was synthesized by co-precipitation method. The desired amount of $\text{MnSO}_4\cdot\text{H}_2\text{O}$, $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ and $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ were dissolved in de-ionized water. The aqueous solution of sodium carbonate was used as the precipitator and an aqueous solution of ammonium

bicarbonate served as the chelating agent (kept around 0.8 mol L^{-1} during the whole precipitation process). The solutions were mixed slowly in a continuously stirred 50 L tank reactor under air atmosphere, and the temperature and pH value of the mixed solution were kept at $55 \text{ }^{\circ}\text{C}$ and 8.0 at **front 3 h** to form the loose core, and then turn pH to 8.5 at next stage (1, 3 and 7 h) to form the compact shell, and the obtained carbonate precursors are named as H1-1, H2-1 and H3-1 (conventional particles: kept at $55 \text{ }^{\circ}\text{C}$ and 8.5 during the program, named as H0-1). The precursors and lithium carbonate were mixed in the molar ratio of $\text{Li}/(\text{Mn}+\text{Ni}+\text{Co})=1.56$, and annealed at $500 \text{ }^{\circ}\text{C}$ for 6 h firstly and $950 \text{ }^{\circ}\text{C}$ for 16 h in air to get the hollow spherical $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ samples which are named as H1, H2 and H3 accordingly (conventional particles named as H0). The **Zr compound** coated hollow spherical $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ (the quality fractions of **Zr compound** is 2%) was prepared by a solution method. Stoichiometric $\text{LiOH}\cdot\text{H}_2\text{O}$ and $\text{Zr}(\text{NO}_3)_2$ in a molar ratio of 2:1 were completely dissolved in absolute ethanol. The sample H2 was added into the solution under vigorous stirring. After evaporating the solvent at $80 \text{ }^{\circ}\text{C}$ for 5h, the obtained powders were calcinated at $500 \text{ }^{\circ}\text{C}$ for 6 h to obtain the **Zr compound** coated hollow spherical $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$.

X-ray diffraction (XRD) and scanning electron microscopy (SEM) are employed to identify the crystalline phase and morphology of the samples. The cross-section views of hollow spherical particles were prepared in an epoxy mount and polished. The electrochemical performance was performed using a two-electrode coin-type cell (CR2025) of $\text{Li} \mid \text{LiPF}_6 (\text{EC}:\text{EMC}:\text{DMC} = 1:1:1 \text{ in volume}) \mid \text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$. Electrode films consisting of the $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode materials are prepared by a slurry coating technique. $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ powder, conductive carbon, and PVDF binder are mixed in a ratio of 8: 1: 1 in N-methylpyrrolidinone (NMP)

solvent and stirred for uniform slurry. The slurry is then coated on an aluminum foil to make the electrode film, followed by drying overnight at 120 °C in an air dry oven. Electrodes are punched in the form of 12 mm diameter disks. A polypropylene micro-porous film is used as the separator. The assembly of the cells is carried out in an argon-filled glove box. The cells are charged and discharged over a voltage range of 2.5-4.6 V versus Li/Li⁺ electrode at current densities of 12.5-250 mA g⁻¹ at room temperature. Inductively coupled plasma (ICP) has been used to test the quantity of Mn dissolve in electrolyte after these electrodes cycled 100 times at 250 mA g⁻¹. Electrochemical impedance spectroscopy (EIS) was utilized to analyze problems of dynamics in the frequency range from 0.1 MHz to 0.01 Hz.

3. Results and discussion

The X-ray diffraction patterns of different Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O₂ cathode materials are given in Fig.1. As it can be seen from Fig.1, all the peaks can be indexed based on the R $\bar{3}$ m structure, except for the peaks between 20° and 25°, those are caused by super-lattice ordering of Li, Mn, Ni and Co atoms in the layered structure with Li₂MnO₃-type character.[22-24] In addition, higher values of $I_{(003)}/I_{(104)}$, at range of 1.923-1.981(which lists in the Table 1), also confirms an ideal structure.[25] Furthermore, as presented in the Table 1, the lattice parameters of conventional and hollow spherical Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O₂ are $a=2.8508$ - 2.8516 Å and $c=14.2007$ - 14.2232 Å, which are consistent with other reports with a small range.[26, 27] Obviously, based on the analysis above-mentioned, conventional and hollow spherical particles all have got similar and nice crystal structure.

Fig. 2 shows surface morphology of these Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O₂ particles, the conventional particles consisting of a number of primary particles have a size of under 2μm, and

the primary particles are easier to forming particles agglomeration, as shown in Fig.2 (a) and (b).

The surface of hollow spherical particles become more compact and smooth with the increase of shell thickness, which may have benefits on the resistance of corrosion from electrolyte.

Furthermore, specific surface areas of H0, H1, H2 and H3 are calculated to be 3.3467, 0.8433, 0.5484 and 0.3994 $\text{m}^2 \text{g}^{-1}$ via the Brunauer-Emmett-Teller (BET) method. Sample H1 own the highest specific surface area around the hollow spherical particles maybe the result of structure collapses of particles, which can be found in the Fig. 2(d), and the structure collapse is most likely due to the shell thickness is too thin to remain structural stability. Therefore, the inner structure and shell thickness of $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ particles have been investigated by cross sections, as illustrated in Fig. 3. As can be seen from Fig. 3, the agglomeration randomly happened among conventional small particles can be proved clearly within broken white lines on the Fig.3 (a), which will results in the distance of lithium ion diffusion have increased. To be more specific, these conventional small particles appearances a strong possibility to forming larger particles with a size ranges in width from 2.3 to 4.2 μm , even more large particles what cannot observed in Fig.3 (a) and (b). The formation of this hollow spherical architecture maybe can explain by a mechanism analogous to the Kirkendall effect.[28] These particles illustrate a hollow spherical architecture, with the shell thickness at range from 1.2 to 2.5 μm . The analysis based on Fig. 2 and Fig. 3 suggests that a firm structure for hollow spherical particles can be obtained when the shell thickness reach to 1.8 μm based on the particles size of 8-10 μm .

As shown in Fig. 4 and Table 2, sample H0, H1, H2 and H3 deliver the specific capacities of 251, 265, 265 and 257 mAh g^{-1} , at 12.5 mA g^{-1} , respectively. Hollow spherical particles show higher discharge capacities than that of conventional particle, which may benefit from the

excellent dispersed state and short diffusion path. But the discharge capacity of hollow spherical particles declined with the shell thickness further increase, especially at high current density (H1 171 vs. H3 159 mAh g⁻¹, at 250 mA g⁻¹). However, as shown in Fig. 5, the cycle performance of sample H1 is unsatisfactory relative to its rate discharge property, the discharge capacity only represents 59.1 % of the initial cycle capacity at 250 mA g⁻¹ after 100 cycles. This unsatisfying cycle performance may be result from the structure collapse of particles, which makes more serious corrosion happened on the surface of particles. As shown in Table 3, the Mn dissolution of all the samples is worse than Ni and Co in the electrolyte, and the dissolved amount of Mn of conventional particles is much higher than that of hollow spherical particles, which own to the highest specific surface area of conventional particles. Additionally, the dissolved amount of Mn of sample H1 is higher than other hollow spherical samples, which may due to the increased specific surface area result from particles collapse, and then leads to a worse cycle performance than sample H2 and H3. However, the cycle performance gets worse with the shell thickness increase, which may due to the increase of electronic and ionic resistance.

Although this hollow spherical structure can help the lithium rich layered oxides to resist the corrosion from electrolyte, because of the low specific surface area they represent. However, these hollow spherical particles still exposed to the corrosive electrolyte directly. Therefore, we further covered these hollow spherical particles with a layer of Li₂ZrO₃, which can be clearly seen from Fig. 6 (c). These surface indentations on the surface of Zr compound coated particles are no longer as noticeable as bare hollow spherical particles, as shown in Fig.6 (b-c). Obviously, the Zr compound coating layer has a slight effect on lattice parameters, but can hardly influence the crystal structure of hollow spherical particles, which can definitely confirmed by Fig.1 and Table 1. As shown in Fig.6

(d-f), reveals that the formed powders are highly crystalline, and a coating layer (about 7.3 nm) can be easily observed on the surface of **Zr compound** coated particles.

As shown in Fig. 7, these materials with different kinds of structure show different trends of capacity fade when the current density increased. When current density as low as 12.5 mA g^{-1} , the distinction of polarization of different materials is inconspicuous, the **Zr compound** coated particles displays a lower reversible capacities than that of bare hollow spherical particles, which may because the capacity contribution of **Zr compound** coating layer can not make up the capacity loss of equal quality lithium rich layered oxides. However, when current density increased from 12.5 to 250 mA g^{-1} , the **Zr compound** coated particle delivers the highest discharge capacity, which may due to the **Zr compound** coating layer can protect the hollow spherical particles away from the corrosive electrolyte, and then effectively prevent the Mn dissolution in electrolyte, as listed in Table 3, which means **Zr compound** coated particles can maintain a good crystal structure during the electrode process. Meanwhile, the **Zr compound** coated particle shows the highest capacity retention, representing 143 mAh g^{-1} after 100 cycles at 250 mA g^{-1} . In sharp contrast, the conventional particle only delivered a much lower discharge capacity of 83 mAh g^{-1} . After 100 cycles at 250 mA g^{-1} , the crystal structures of those three materials have been investigated by HRTEM, as shown in Fig.6 (g-i). Obviously, the crystal structure of conventional articles become unordered, and the distance between two lattice fringes become widening after these cycles. Although, about hollow spherical particles, the crystal structure of some region area become unordered, pointed out by the arrow and circle in Fig.6 (h) marked number 1, 2. Even so, the performance of hollow spherical particles is better than the small amorphous particles[21], because partial region of the material remains integrity crystal structure, which ensures a better

electrochemical properties of hollow spherical particles. Furthermore, as illustrated in Fig.6 (i), this Zr compound coating layer can effectively prevent these crystal structure changes during the electrode process, which may be the direct reason for Zr compound coated particle to represent the best electrochemical properties.

To gain insight into the reason that these three different particles display different electrochemical properties, the electrochemical impedance spectroscopies (EIS) of these $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ particles are measured, and these obtained plots consist of a semicircle arc and a straight line, which are attributed to the charge transfer process and the lithium diffusion process in the oxide structure, respectively.[29, 30] These plots are well fitted using the electric equivalent circuit shown in the inset figure of Fig. 8(a). In the equivalent circuit, R_s and R_{ct} represent the solution resistance and charge-transfer resistance, respectively. CPE is related to the double layer capacitance and passivation film capacitance. Z_w represents the Warburg impedance (Z' is the real impedance and Z'' is the imaginary impedance). The parameters of the equivalent circuit are listed in Table 4. Additionally, those exchange current densities (i^0) are calculated by the formula ($i^0 = RT/nFR_{ct}$, where n is the number of transferred electrons) and list in Table 4. Obviously, the solution resistances are very similar and small, and the Zr compound coated particles shows the lowest charge transfer resistance, which may benefited from the coefficient of hollow spherical structure and Zr compound coating layer. Additionally, the charge transfer resistance increased with the shell thickness increase and the trend of lithium ion diffusion coefficient changed in opposite direction. The plots of the real axis Z_{re} vs. the reciprocal square root of the lower angular frequencies $\omega^{-0.5}$ are illustrated in Fig. 8(b).[31, 32] This relation is governed by Eq. (1). According to Fig. 8(b) and Eq. (2), the slope of the straight lines represents

the values of Warburg impedance coefficient (σ_w , list in Table 4). The diffusion coefficients (D) of the lithium ions diffusing into the bulk electrode materials are calculated using Eq. (2) and recorded in Table 4. Notably, sample H1 show the lowest resistance for lithium ion diffusion process owing to its shortest diffusion length, as shown in Fig.3. In addition, this hollow spherical structure has a greater influence on lithium ion diffusion coefficient than charge transfer resistance. Specifically, the lithium ion diffusion coefficient of conventional particles is 7.43×10^{-16} , and the hollow spherical structure help to raise these lithium ion diffusion coefficients to (H1) 8.92×10^{-15} , (H2) 4.16×10^{-15} and (H1) $3.70 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$, and Zr compound coating layer can further modificate the electronic and ionic transmission capacities to some extent at the same time. Furthermore, after 100 cycles at 250 mA g^{-1} , the charge-transfer resistance of pristine materials increase shapely to $806.60 \text{ } \Omega$ and lithium ion diffusion coefficient decrease remarkably to $2.01 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$, as illustrated in Fig. 9 and Table 4. On the contrary, the hollow spherical structure and Zr compound coating layer can effectively prevent the deterioration of electronic and ionic transmission capacity, which are in good agreement with the analysis of HRTEM analysis above. Therefore, based on the discussion mentioned above, a surface modification combine with the design of hollow spherical structure with an appropriate shell thickness can effectively enhance these electrochemical properties of lithium ion layered oxides.

$$Z_{re} = R_s + R_{ct} + \sigma_w \cdot \omega^{-0.5} \quad (1)$$

$$D = 0.5 \left(\frac{RT}{AF^2 \sigma_w C} \right)^2 \quad (2)$$

Where ω , angular frequency region; R, the gas constant; T, the absolute temperature; F, Faraday's constant; A, the area of the electrode surface; and C, molar concentration of Li^+ ions.

4. Conclusion

In summary, the lithium rich layered oxides with different morphologies are synthesized by co-precipitation followed by calcination. The hollow spherical structure can markedly decrease the specific surface area of lithium rich layer oxides, and then weaken the Mn dissolution in corrosive electrolyte. In addition, the thinner the shell thickness is, the higher the electronic and ionic conductivities are, which bring a better rate capacity to hollow spherical $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ particles. However, the structure of hollow particles becomes fragile when the shell thickness smaller than 1.8 μm , which should result in a bigger specific surface area that means more corrosion from electrolyte. Further modified the surface of hollow spherical particles with **Zr compound** can improve the electronic and ionic transmission capacities to some extent at the same time. This study shows that an appropriate surface modification based on the optimal structure design is significant in the development of lithium rich manganese layered oxides.

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Table captions

Table 1 Lattice parameters of conventional, hollow spherical and Zr compound coated particles

Table 2 The rate capacities of conventional and hollow spherical particles

Table 3 Mn dissolution of conventional, hollow spherical and Zr compound coated particles

Table 4 The impedance parameters of conventional, hollow spherical and Zr compound coated particles before and after cycles

Figure captions

Fig. 1 XRD patterns of conventional, hollow spherical and Zr compound coated particles

Fig. 2 SEM images of (a-b) conventional particles: H0, hollow spherical particles: (c-d) H1, (e-f) H2 and (g-h) H3

Fig. 3 Cross sections of (a-b) conventional particles: H0, hollow spherical particles: (c-d) H1, (e-f) H2 and (g-h) H3

Fig. 4 Typical charge-discharge curves of conventional and hollow spherical particles

Fig. 5 Cycle properties of conventional and hollow spherical particles

Fig. 6 SEM images of (a) conventional particles: H0, (b) hollow spherical particles: H2 and (c) Zr compound coated particles: HZ; HRTEM image of conventional particles (d)/(g), hollow spherical

particles (e)/(h) and **Zr compound** coated particles (f)/(i) before and after 100 cycles at 250 mA g⁻¹

Fig. 7 Discharge capacities and cycle properties of conventional (H0), hollow spherical (H2) and **Zr compound** coated particles (HZ)

Fig. 8 (a) AC impedance measurement of conventional, hollow spherical and **Zr compound** coated particles before electrode process, the inset figure shows the equivalent circuit for the plot fitting, (b) Plots of Z' vs $\omega^{-1/2}$ of conventional, hollow spherical and **Zr compound** coated particles

Fig. 9 (a) AC impedance measurement of conventional, hollow spherical and **Zr compound** coated particles after 100 cycles at 250 mA g⁻¹, (b) Plots of Z' vs $\omega^{-1/2}$ of conventional, hollow spherical and **Zr compound** coated particles

Table 1

Samples	$a(\text{\AA})$	$c(\text{\AA})$	c/a	$I_{(003)}/I_{(104)}$
H0	2.8510	14.2232	4.989	1.953
H1	2.8516	14.2179	4.986	1.923
H2	2.8510	14.2042	4.982	1.981
H3	2.8508	14.2007	4.981	1.974
HZ	2.8813	14.0937	4.892	1.967

Table 2

Samples	12.5 mAg ⁻¹	25 mAg ⁻¹	50 mAg ⁻¹	125 mAg ⁻¹	250 mAg ⁻¹
H0	251	235	209	179	152
H1	265	248	224	198	171
H2	265	253	231	197	170
H3	257	241	215	184	159

Table 3

Samples	Mn (ppm)	Co (ppm)	Ni (ppm)
H0	101.95	16.77	22.50
H1	42.89	3.24	5.16
H2	37.20	2.13	4.97
H3	35.72	1.98	3.55
HZ	10.81	0.02	0.33

Table 4

Samples	R_s (Ω)	R_{ct} (Ω)	σ_o ($\Omega\text{cm}^2\text{s}^{-0.5}$)	$D(\text{cm}^2\text{s}^{-1})$	I^0 (mA cm^{-2})
H0	6.51	136.00	102.03	7.43×10^{-16}	1.89×10^{-4}
H1	3.36	87.0	29.43	8.92×10^{-15}	2.95×10^{-4}
H2	2.54	154.80	43.10	4.16×10^{-15}	1.66×10^{-4}
H3	3.61	330.2	144.50	3.70×10^{-16}	7.78×10^{-5}
HZ	3.51	64.20	36.20	5.90×10^{-15}	4.00×10^{-4}
H0 (after 100 cycles)	6.48	806.60	195.93	2.01×10^{-16}	3.18×10^{-5}
H2 (after 100 cycles)	11.18	727.00	169.00	2.71×10^{-16}	3.58×10^{-5}
HZ (after 100 cycles)	12.37	404.80	100.12	7.71×10^{-16}	6.34×10^{-5}

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9