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Core-shell Architecture Strategy of Improving the Electrochemical Performance of the Li-rich Layered Oxides: A Review

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Abstract. Lithium-ion battery (LIB) serves as power supply for suitable electronics and stationary electrical systems (storage) as a result of their outstanding combination of extraordinary densities (power and energy). The cathode constitutes an integral part of LIBs and its property determines the performance of the battery. The layered lithium-rich oxide (LLO) is unique and favourable cathode materials for LIBs as a result of its high capacity compared to conventional cathode materials such as LiNiO_2 etc. However, they demonstrate several performance limitations such as low first cycle efficiency and poor cycling stability thus, limiting their practical applications. Therefore, this review discussed a core-shell architecture strategy of enhancing the electrochemical performance of the LLOs materials for LIBs.

Keywords: LLOs materials, Lithium-ion batteries, Core-shell architecture

1. Introduction

Renewable energy serves as an alternative and favourite source of energy to non-renewable energy because they are infinite in quantity, clean, natural and reduces greenhouse gases in the atmosphere and other environmental pollution [1]. However, by nature, they are constrained by their intermittency. Consequently, for a continuous energy supply and availability, it is highly imperative to store the excess energy generated from renewable energy [2].

Lithium-ion batteries are the best backup device or storage device for renewable energy as a result their unequalled power and energy densities, non-memory effect and better portability compared to other storage devices such as Ni-MH batteries, Pb-acid batteries, Ni-Cd batteries [3]. LIBs consist of three major components, namely the electrolyte, anode and cathode. Of all the three components, the cathode determines the battery performance [3,4,5,6]. Several studies have been conducted on enhancing the cathode material [3,4,]. The first saleable cathode material is lithium cobalt oxide (LiCoO_2). It has 273 mAh/g theoretical capacity but the transition metal redox reaction during charge-discharge cycles limited the actual capacity to 150 mAh/g [7].

Recently, an advancement on the aforementioned cathode materials led to the layered lithium-rich oxides (LLOs; $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiTMO}_2$, TM = Nickel, Manganese, Cobalt) synthesis. It is one of the desirable cathodes for extraordinary densities system. For example, an extensive storage devices used LIBs as a result of its extraordinary capacity and high working potentials $> 3.8\text{V}$ (vs. Li^+/Li^0) [8,9]. The high capacity observed in comparison with other conventional, spinel and olivine cathode materials could be credited to transition metals cationic and oxygen anionic redox reactions, which resulted in a high amount



of lithium-ion intercalation/deintercalation during the charging and discharge process which in turn increase the storage capacity of the host material [7].

2. Crystal structure of LLOs

The structure of LLOs could be grouped into $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiMO}_2$ two-phase model and $\text{Li}(\text{Li}_x\text{M}_{1-x})\text{O}_2$ single-phase model [10,18]. The two-phase model is considered as a composite where a monoclinic phase Li_2MnO_3 ($C/2m$ space group) is integrated with a rhombohedral LiMO_2 ($R\bar{3}m$ space group) at the atomic level on the account of the identical O3-type layered structure as shown in Figure 1a. More so, the closed packed layer distance in the plane (001) of Li_2MnO_3 monoclinic phase and plane (003) of LiMO_2 rhombohedral phase is the same (~ 4.9 Å). Thus, at the atomic level, the two phases are compatibly integrated. The single-phase model is considered as a model (solid solution) with a homogenous long-range ordering with either $C/2m$ single-phase or $R\bar{3}m$ single phase as shown in figure 1b [10, 23].

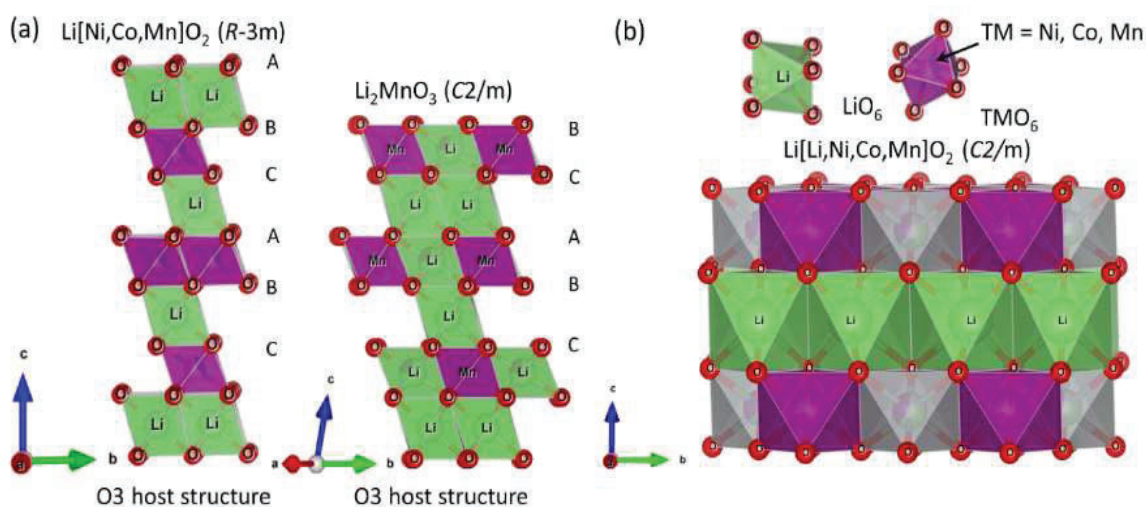


Figure 1. (a) Rhombohedral and monoclinic phase ($R\bar{3}m$ & $C2/m$), and (b) $\text{Li}(\text{Li}_x\text{M}_{1-x})\text{O}_2$ monoclinic phase Source: [7]

3. Challenges of LLO materials

The layered lithium-rich oxides cathode materials deliver higher capacity, good thermal stability and their cost of production are low compared to conventional cathodes such as lithium cobalt oxide, but they exhibit several performance limitations that affect their commercialization and application.

These limitations are connected to their underlying mechanistic reactions, chemical and structural evolution [10,18,19]. The limitations are relatively low rate capability caused by poor ionic and poor electronic conductivities of Li_2MnO_3 components; low initial coulombic efficiency (78-80 %) lower than conventional cathode material or spinel cathode materials caused by cainitial irreversible capacity loss (IRCL); fading (voltage and capacity) due to layer to spinel evolution or structural changes and O redox activity during cycling.

Their limitations lower the power density and energy efficiency of the battery and complicate the battery management systems. Thus, limiting their practical application [5, 6, 8, 9, 11, 12,]

4. Improving LLO materials via synthesis by core-shell structure

Conventionally, the LLOs are synthesized as an intergrowth of both LiMO_2 ($M = 3d$ -transition metals) $R\bar{3}m$ rhombohedral and Li_2MnO_3 $C2/m$ monoclinic phases. Both phases are integrated structurally and not controlled during their synthesis like the core-shell structure (CS) but are randomly dispersed within the particle forming a heterostructure composite [11].

Recently, studies have shown the LLOs electrochemical performance can be improved by synthesizing it in form of a core-shell (CS) configuration. The Nickel-rich oxide layer serves as the core (C) and Manganese-rich oxide layer serves as the shell (S) as shown in Figure 2. In this structure, the Ni-rich layered core is accountable for the high capacity of the material. Conversely, it gives poor thermal stability and cycling instability because of its active catalytic surface. The Mn-rich layered oxide shell is responsible for the stability of the material (thermal stability). Thus, the CS like structure counterbalance the weaknesses of both the core and the shell materials. [8,9,13].

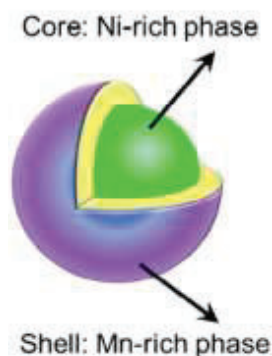


Figure 2. Schematic diagram of layered lithium-rich oxide cathode CS structure Source: [25]

Sun *et al.*, (2009) reported a microscale CS $\text{Li}[(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})_{0.8}(\text{Ni}_{0.5}\text{Mn}_{0.5})_{0.2}] \text{O}_2$ configuration synthesis. The study revealed the CS like configuration of this material is responsible for its improvement in terms of stability (i.e thermal) and discharge capacity compared with conventional cathode material [14]. Also, Ju and Ryu (2010) investigated the synthesis of $\text{Li}[(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})_{0.8}(\text{Ni}_{0.5}\text{Mn}_{0.5})_{0.2}] \text{O}_2$ CS through coprecipitation route. The synthesised material was analysed with XRD, SEM, FE-SEM, EIS and DSC and it shows better thermal stability, cyclic performance and safer in comparison with the core structure. The thermal stability was credited to the shell which restrained the oxygen loss from the lattice [15].

Yang *et al.*, (2013) improved $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}] \text{O}_2$ material stability by coating active Li_2MnO_3 on it during synthesis to form a $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2\text{-Li}_2\text{MnO}_3]$ CS materials via simple sol-gel method. They reported that the improved properties of the CS material in comparison with $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}] \text{O}_2$ was credited to the shell. It prevented the core component from right contact with the electrolyte, therefore no structural disruption was observed during cycling at high temperature [16].

Noh *et al.*, (2014) investigated the synthesised of nanostructured $y\text{Li}_2\text{MnO}_3 \cdot (1-y) \text{LiMO}_2$ (M=Ni, Mn and Co) CS materials via the mechanochemical ball-milling method. Their result revealed that the performance of the synthesised material was higher compared to the nickel rich core material. They hypothesised that the core LiMO_2 (nickel rich) is accountable for high specific capacity and the shell Li_2MnO_3 is accountable for the stability of the cell by checkmating the nickel detrimental effect on the material surface. Li *et al.*, (2015) also reported better electrochemical performance of LLO CS material over the core-only material and the shell-only material. The improvement was also accounted to the balance amid the strengths and the weaknesses of the core and shell material in the hybrid (CS) system [8].

Kim *et al.*, (2016) improved the performance of $\text{LiNi}_{0.44}\text{Mn}_{0.32}\text{Co}_{0.24}\text{O}_2$ by modifying the surface with stabilized Li_2MnO_3 as a result of high atomic-level structural compatibility. The Li_2MnO_3 suppressed the layered-spinel phase evolution excellently compared to previous coating materials; therefore, it provided faster diffusion for Li-ion [17]. Consequently, it solved the capacity fade and voltage fade problem of LLOs.

Furthermore, Chong *et al.*, (2017) synthesized a spherical $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2 @ \text{Li}_{1.2}\text{Ni}_{0.4}\text{Mn}_{0.4}\text{O}_2$ CS structure composition via in-situ hydrothermal method. The material was characterized with XPS, SEM and EDS and their result confirmed an excellent growth of the core-shell structure and it showed some better electrochemical properties [18].

Kong *et al.*, 2019 synthesised cross-linked nanorods and agglomerate microrods structural LLOs cathode materials via two different MnO_2 templates strategies (nanowires and nanorods) to control the structure and the particle size of the electrode material which in turn determines the cathodes electrochemical performance. The cross-linked structural material showed a better electrochemical properties compared to agglomerate microrods structural materials because it provides an internal cavity, shorter diffusion length for lithium ions and larger reaction surface [19].

Ma *et al.*, (2019) comparatively studied the coatings of a shell ($\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$) on core ($\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$) via simple and concentration gradient shell (CGS) coating methods. The CGS core-shell (CS) cathode showed a better electrochemical property in comparison with the simple CS cathode. It was attributed to the uniformity between the shell and core at the atomic level compared with the simple CS cathodes. In addition, a cracked shell was observed for the simple core-shell during cycling due to its distinct core-shell structure [20].

Ehi-Eromosele *et al.*, (2020a) studied the properties of composite and CS architecture of $0.5\text{Li}_2\text{MnO}_3-0.5\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ cathode via solution combustion-mechanochemical synthesis route. The CS architecture showed a better performance compared to the composite architecture. The performance was due to the limited structural change and lower surface reactivity during electrochemical cycling in the CS samples. This was attributed to the screening of $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ (Nickel-rich core) from reacting with the electrolyte and air by Li_2MnO_3 (Manganese-rich shell). In addition, XAS data revealed that higher volumetric changes and incomplete reduction of Nickel were observed respectively, which led to severe degradation for the composite sample. This, in turn, validated the electrochemical performance data [21]. Furthermore, Ehi-Eromosele *et al.*, (2020b) reported similar cycling stability for both the composite and CS structure. However, the CS structure gave better thermal stability, rate performance, higher coulombic efficiency and discharge capacity compared to the composite structure. Thus, the CS architecture improved the LLO cathodes electrochemical and structural performance [22].

Maeng *et al.*, (2020) synthesized a CS architecture through a co-precipitation route in which the $\text{LiNi}_{0.9}\text{Mn}_{0.05}\text{Co}_{0.05}\text{O}_2$ is the core and the $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ is the shell. The electrochemical and structural performance of the CS structure revealed improved capacity retention, mechanical strength and thermal stability compared with the commercial homogenous composition ($\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$). The better electrochemical performance was attributed to higher stiffness, compressive stress-strain and stronger binding force, which prevented crack formation during cycling, compared with commercial materials [24]. In addition, Hua *et al.*, (2020) reported on core-shell layered structure Li-ion (de)intercalation mechanism during electrochemical cycling. Their work revealed that the Ni-rich phase core contributed to the first capacity compared with the shell. However, the Mn-rich phase shell contributed more to the structural stability of the cathode material [25].

5. Conclusion

Synthesis of LLO in form of core-shell architecture has been proved as an effective approach to improving or enhancing its electrochemical performance. Researchers have hypothesised that the coulombic efficiency (CE), rate capability (RC) and capacity retention of LLO materials can be improved by minimizing the irreversible Li and O loss from the Li_2MnO_3 shell component, restricting electrolyte oxidation and improving the interface stability between the electrode and the electrolyte.

6. Conflicts of Interest

The authors declare no conflicts of interest.

7. Acknowledgements

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