



Electrochemical properties of yolk-shell structured layered-layered composite cathode powders prepared by spray pyrolysis



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ABSTRACT

Layered-layered yolk-shell powders with composition $0.6\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2 \cdot 0.4\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ are first formed as an intermediate product near the reactor entrance by drying and decomposition of droplets. Combustion, contraction, and recombination processes of intermediate product produce yolk-shell-structured powders. The yolk-shell structure of the powders prepared directly by spray pyrolysis is maintained even after post-treatment at 800°C ; this treatment temperature yields the best electrochemical performance. The composition of the powders post-treated at 800°C is $\text{Li}_{1.12}\text{Ni}_{0.14}\text{Co}_{0.14}\text{Mn}_{0.59}\text{O}_2$. Mean grain sizes of the yolk-shell $0.6\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2 \cdot 0.4\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powders, post-treated at 700, 750, and 800°C , measured from high resolution TEM images, are 47, 54, and 79 nm, respectively, and their BET surface areas are 14, 9, and $7\text{ m}^2\text{ g}^{-1}$. The initial discharge capacities of the powders, post-treated at the above temperatures, are 188, 280, and 239 mA h g^{-1} , respectively, and their initial Coulombic efficiencies are 87, 80, and 78%. Discharge capacities after 50 cycles of the post-treated powders are 81, 194, and 183 mA h g^{-1} , respectively, and the corresponding capacity retentions are 43, 70, and 77%.

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1. Introduction

$\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2$ -stabilized cathodes with composite structures have become attractive because of their high discharge capacity, greater than 200 mA h g^{-1} , and their enhanced safety at high voltages, i.e. over 4.5 V [1–14]. The $\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2$ component stabilizes the electrode structure and enhances the discharge capacity by extracting lithium, concomitant with release of oxygen [11,12]. The advantages of the $\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2$ component, including its influence on structural stability and electrochemical properties of layered $x\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2 \cdot (1-x)\text{LiMO}_2$ electrodes, have been proposed and investigated by many research groups [1–14].

Recently, there has been much interest in special structures with distinctive core@void@shell configuration, which are commonly called a yolk-shell structure, because of their many potential applications [15–26]. Since yolk-shell structures contain movable

cores and interstitial hollow spaces, they are expected to have great potential for applications in lithium secondary batteries [23–26]. However, in the area of efficient cathodes for LIBs, yolk-shell structured materials have scarcely been studied [25–28]. In general, lithium-metal oxides for LIBs should be post-treated at high temperatures for several hours to achieve high crystallinity and phase homogeneity, in order to provide good electrochemical properties. However, post-treatment at high temperature could lead to destruction of the yolk-shell structure. To the best of our knowledge, a suitable process for preparing $x\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2 \cdot (1-x)\text{LiMO}_2$ yolk-shell powders has not yet been reported.

More recently, a facile, continuous preparation process for yolk-shell structured powders was developed by Kang et al. [27–30]. One particle with yolk-shell structure was formed from one droplet containing metal salt precursors and carbon source material. The formation of metal oxide-carbon composite as an intermediate product was a key factor in the preparation of the yolk-shell structured material by one-pot spray pyrolysis process. The spray pyrolysis process has been successfully applied to the preparation of the yolk-shell structured materials with various compositions. In this study, for the first time, the layered-layered $0.6\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2 \cdot 0.4\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ yolk-shell

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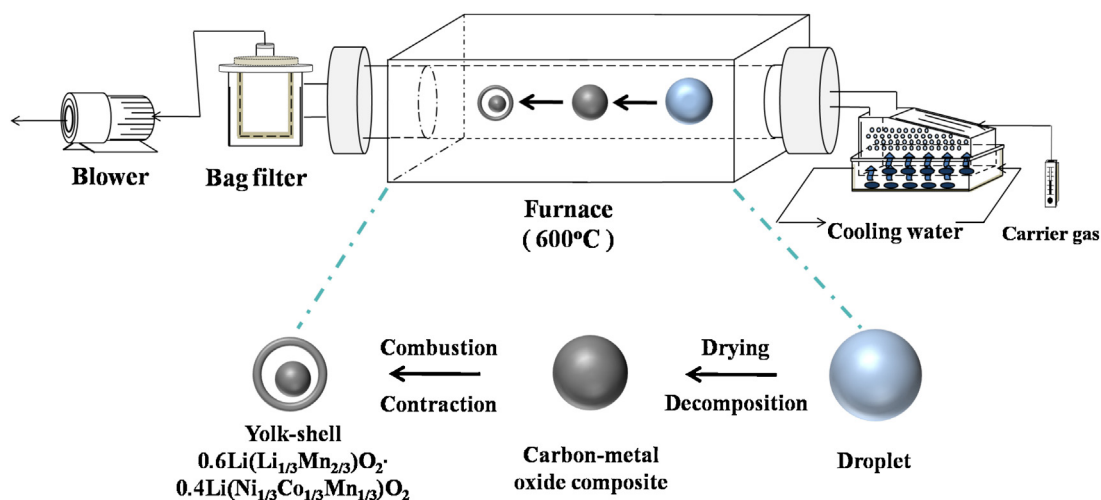


Fig. 1. Schematic diagram of the ultrasonic spray pyrolysis system and the formation mechanism of the yolk-shell powders.

powders were prepared directly by a spray pyrolysis process at 600 °C. The yolk-shell structure of the precursor powders were maintained even after post-treatment at a high temperature of 800 °C. Electrochemical properties of the yolk-shell $0.6\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2 \cdot 0.4\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powders post-treated at various temperatures were investigated.

2. Experimental

2.1. Material synthesis

Yolk-shell $0.6\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2 \cdot 0.4\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powders were prepared directly by ultrasonic spray pyrolysis using a spray solution with sucrose as the carbon source. A schematic diagram of the ultrasonic spray pyrolysis system used for the yolk-shell powders is shown in Fig. 1. A quartz reactor with a length of 1,200 mm and a diameter of 50 mm was used; reactor temperature was maintained at 600 °C, and the flow rate of air used as carrier gas was 10 L min^{-1} . An aqueous spray solution was prepared by dissolving LiNO_3 (Junsei, 98%), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Junsei, 98%), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Junsei, 97%), and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Junsei, 97%) in distilled water. The amount of lithium added to the spray solution was in excess of 3 wt% of the stoichiometric amount needed to facilitate the formation of $0.6\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2 \cdot 0.4\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powders. Total concentration of the Li, Ni, Co and Mn components dissolved in distilled water was 0.5 M. The concentration of sucrose used as the carbon source material was fixed at 0.7 M. The precursor powders obtained by spray pyrolysis were post-treated at temperatures of 700, 750, and 800 °C for 3 h in air atmosphere.

2.2. Characterizations

Crystal structures of the powders were investigated by X-ray diffractometry (XRD) (X'pert PRO MPD), using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$). Morphological characteristics of the powders were investigated using scanning electron microscopy (SEM, JEOL JSM-6060) and high-resolution transmission electron microscopy (HR-TEM, JEOL-2100F). Elemental compositions of the yolk-shell $0.6\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2 \cdot 0.4\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powders were investigated using an inductively coupled plasma-optical emission spectrometer (ICP-OES, Perkin Elmer, OPTIMA 4300 DV). Surface areas of the powders were measured by the Brunauer–Emmett–Teller (BET) method with N_2 used as the adsorbate gas.

2.3. Electrochemical measurements

The electrode was fabricated using a mixture containing 70 wt% active material, 20 wt% activated carbon, and 10 wt% sodium carboxymethyl cellulose (CMC) binder. The size of the electrode was $1\text{ cm} \times 1\text{ cm}$ and the mass loading was approximately 1.6 mg cm^{-2} . Lithium metal and a microporous polypropylene film were used as anode electrode and separator, respectively. The electrolyte was 1 M LiPF_6 in a 1:1 mixture by volume of ethylene carbonate/dimethyl carbonate (EC/DMC). The entire cell was assembled in a glove box under an argon atmosphere. Charge/discharge characteristics of the samples were determined by cycling in the potential range 2–4.8 V at a constant current density of 20 mA g^{-1} using a coin cell.

3. Results and discussion

A schematic diagram for the formation mechanism of the yolk-shell $0.6\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2 \cdot 0.4\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powders is presented in Fig. 1. Metal oxides-carbon composite powders are first formed as an intermediate product near the reactor entrance by drying and decomposition of droplets. The carbon component is formed by polymerization and carbonization of sucrose. Combustion, contraction, and recombustion processes of the carbon component occur in a step-by-step manner as the metal oxides-carbon composite intermediate progresses through the reactor, finally producing yolk-shell-structured powders [29,30]. Morphology and elemental mapping images of the yolk-shell $0.6\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2 \cdot 0.4\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ precursor powders, prepared directly by spray pyrolysis, are shown in Fig. 2. As shown in Fig. 2a, the powders have a spherical shape and yolk-shell structure, a special structure with a distinctive core@void@shell configuration. To further understand the morphology of the particles that compose the powders, high-resolution TEM and elemental mapping images were also investigated, as shown in Fig. 2b–d. The TEM image clearly shows the porous core and shell structures. The shell thickness and diameter of the core of the powder as shown in Fig. 2b were 20 nm and $1.1\text{ }\mu\text{m}$, respectively. The HR-TEM image in Fig. 2c shows the crystalline structure; the clear lattice fringes separated by 0.47 nm, shown in the inset image of Fig. 2c, correspond to the (003) crystal plane of the hexagonal layered structure. The elemental mapping images show uniform distributions of Ni, Co, and Mn components over the powder. The BET surface area of the yolk-shell $0.6\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2 \cdot 0.4\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ precursor powders prepared directly by spray pyrolysis was $14\text{ m}^2\text{ g}^{-1}$.

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