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Continuous Solid-Solution Particle of Cathode Material for Rechargeable Lithium Batteries

H.-J. Noh[a] **and Y.-K. Sun**[a]

[a] *Department of Energy Engineering,*
Hanyang University, Seoul 133-791, Republic of Korea

Introduction

Nickel-rich cathode materials, such as $Li[Ni_{1-x}M_x]O_2$ ($x \leq 0.2$ and M = Co and Mn), are known to deliver high capacity of 200 mAh g^{-1}.[1] However, the unstable structure at the highly delithiated state gives rise to reaction with the organic electrolyte and carbon anode, causing severe safety problems.[2] A great deal of research has been conducted to eliminate such catastrophic effects by developing flame-retardant additives, thermally stable anodes, and thermally stable cathodes.[3] One of the most effective ways to address the safety concern is to coordinate the Ni-rich materials with tetravalent Mn-containing oxide materials, like $Li[Ni_{1/2}Mn_{1/2}]O_2$ or $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$, by forming a core-shell particle or a core-shell particle with concentration gradient in the shell.[4] Tomograms of these core-shell and core-shell concentration gradient particles revealed that $Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O_2$ appeared only in the core, and the delivered capacity was mainly due to the core because the outer shell usually possesses the rate-limiting properties (poor Li + diffusion). It was anticipated that, if the higher concentration of Ni can be maintained from the particle center to the surface, and at the same time the outer surface can be modified by tetravalent Mn, the resulting capacity can be further improved compared to the above two concepts. In addition, the tetravalent Mn in the surface part is responsible for the satisfactory thermal properties. Figure 1 represents the above hypothesis schematically: i) high concentration of Ni (80%) is maintained throughout the spherical particle and ii) the Co content at the center (10%) is gradually reduced to the outer surface (2%), but Mn replaces the reduced Co content, forming a solid solution in the particle.

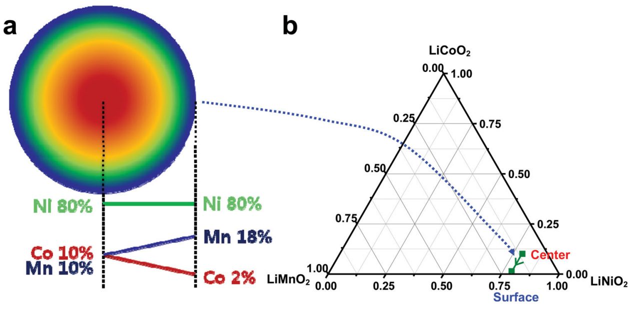

Figure 1. a) Schematic drawing solid-solution particle and b) the resulting phase diagram showing continuous variation in composition, represented by the tie line of $Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O_2$ (center part) to $Li[Ni_{0.8}Co_{0.02}Mn_{0.18}]O_2$ (surface part).

Experimental

The Ni-fixed full gradient structure formation of $[Ni_{0.8}Co_{0.2}](OH)_2$ inner particles, Co-free aqueous solution was prepared by mixing required amounts of $NiSO_4$ and $MnSO_4$ salt solutions (Ni:Mn = 0.8:0.2 in molar ratio) and Mn-free (Ni:Co = 0.8:0.2 in molar ratio) solution separately. Initially, Co-free aqueous solution was slowly pumped into the stoichiometric amount of Mn-free solution, and at the same time, the homogeneously mixed solution, containing Ni, Co, and Mn ions, was fed into the CSTR. After a certain reaction time, green Ni-fixed full gradient particles slowly accumulated. The coprecipitated precursor powders were filtered, washed, and dried at 110 °C And that compounds were thoroughly mixed with $LiOH \cdot H_2O$ and heated at 750 °C for 10h in air, respectively. The chemical compositions of the resulting powders were determined by atomic absorption spectroscopy (AAS, Vario 6, Analyticjena). Line scans for the full-gradient materials were obtained with an electron probe X-ray microanalyzer (EPMA, JXA-8100, JEOL).

Results and discussion

Figure 2 shows a cross-sectional scanning electron microscopy (SEM) image of a single lithiated solid solution particle (SSP) $Li[Ni_{0.80}Co_{0.07}Mn_{0.13}]O_2$ oxide particle and the corresponding elemental distribution of Ni, Co, and Mn. Taken together, these results describe a solid solution with a composition between $Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O_2$ and $Li[Ni_{0.8}Co_{0.02}Mn_{0.18}]O_2$ (see tie line in Figure 2). The total average composition of the solid solution particle (SSP) was found to be $Li[Ni_{0.8}Co_{0.06}Mn_{0.14}]O_2$, determined by atomic absorption spectroscopy (AAS).

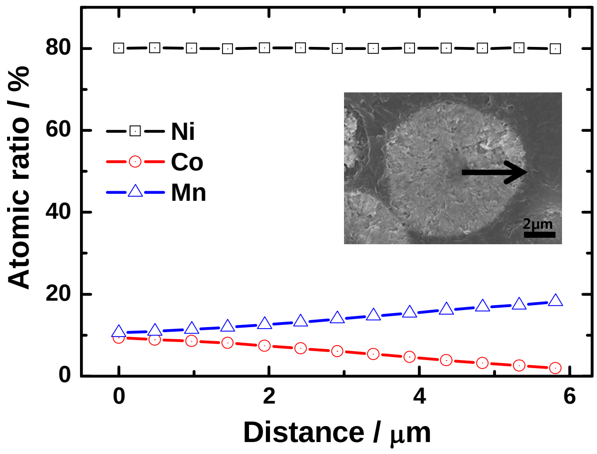

Figure 2. SEM and electron-probe X-ray micro-analysis results for SSP $Li[Ni_{0.8}Co_{0.06}Mn_{0.14}]O_2$.

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