Polyimide Gel Polymer Electrolyte-Directed Nanoscale Wrapping of High-Voltage $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ Cathode Active Materials for Lithium-Ion Batteries

Polyimide Gel Polymer Electrolyte-Directed Nanoscale Wrapping of High-Voltage $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ Cathode Active Materials for Lithium-Ion Batteries

Jang-Hoon Park, Ju-Hyun Cho, Sang-Young Lee[1,*]

Department of Chemical Engineering, Kangwon National University, Chuncheon, Kangwondo, 200-701, Korea

A new and facile approach for the surface modification of high-voltage $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode active materials is demonstrated. This strategy is based on polyimide (PI) gel polymer electrolyte (GPE)-directed nanoscale wrapping. The PI coating layer successfully wraps a large area of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ surface via thermal imidization of (pyromellitic dianhydride/ oxydianiline) polyamic acid. Salient features of the PI wrapping layer are the highly-continuous surface coverage with nanometer thickness (~ 10 nm) and the facile ion transport through the nanoscale PI layer. Based on a sound understanding of the nanoarchitectured PI wrapping layer, its influence on the cell performance and thermal stability of high-voltage $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ is investigated as a function of charge cut-off voltage (herein, 4.6 and 4.8 V). The anomalous PI wrapping layer substantially improves the high-voltage cycling performance and alleviates the interfacial exothermic reaction between delithiated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and liquid electrolyte. These results demonstrate that the PI wrapping layer effectively prevents the direct exposure of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ surface to liquid electrolytes that are highly vulnerable to electrochemical decomposition at high charge voltage conditions, thus behaving as a novel ion-conductive protection skin that mitigates the unwanted interfacial side reactions.

References
[1] Li, H.; Wang, Z.; Chen, L.; Huang, X. *Adv. Mater.* **2009**, 21, 4593.
[2] Liu, C.; Li, F.; Ma, L. P.; Cheng, H. M. *Adv. Mater.* **2010**, 22, E28.
[3] Palacin, M. R. *Chem. Soc. Rev.* **2009**, 38, 2565.
[4] Whittingham, M. S. *Chem. Rev.* **2004**, 104, 4271.
[5] Goodenough, J. B.; Kim, Y. *Chem. Mater.* **2010**, 22, 587.

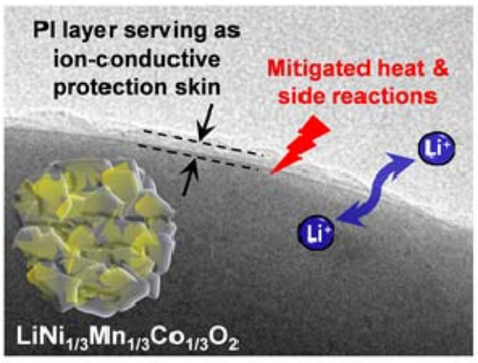

Fig. 1. A TEM photograph of PI-wrapped $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$. The insets indicate schematic illustrations of nanoarchitectured PI wrapping layer formed onto $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and its function as an ion-conductive protection skin to suppress the unwanted interfacial side reactions.

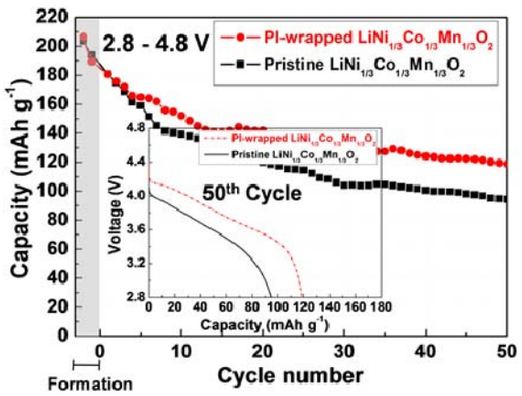

Fig. 2. Discharge capacities (charge/discharge current density = 1.0 C/1.0 C) as a function of cycle number for cells assembled with pristine or PI-wrapped $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ under a voltage range between 2.8 - 4.8 V. The inset indicate the discharge profiles of cells after the 50^{th} cycle at a given voltage range.