Electrochemical Preparation of Iron Phosphide Anodes for Lithium Secondary Battery

In-Tae Park and Heon-Cheol Shin

School of Materials Science and Engineering Pusan National University Busandaehak-ro 63beon-gil, Geumjeong-gu Busan 609-735, Republic of Korea

Anode materials with the specific capacity higher than that of the graphite have long been desired by the manufacturers of lithium secondary battery and batteryoperated systems (*e.g.* portable electronic devices and electric vehicles). Transition metal phosphide is one of the promising candidates as high performance anode material since it reacts with large amounts of lithium at relatively low potential and a narrow potential range. However, poor cycling stability still remains as an obstacle to its practical use although some works have reported that particular metal phosphide compounds might show the remarkable capacity retention.

A wide variety of metal phosphides M_xP_y (M=Mn, Ti, Fe, Co, Ni, etc) have been synthesized in powder form by solid-state reaction or mechanochemical method and tested as the anode in lithium secondary battery. In spite of much effort, however, it looks like there is little consensus, as far as we know, regarding the capacity fade mechanism of metal phosphide (or phosphorus) electrodes. The absence of proper analysis of degradation mechanism might be due mainly to the use of the phosphide-based composites consisting of phosphide particles and the additives for conduction and binding: the response signal from the phosphide itself might be seriously altered by the presence of additives and the porous nature of composite electrode. Furthermore, such a distortion of the response signal makes right evaluation of the electrochemical properties quite unlikely. In this respect, additive-free pure phosphide films might be ideally suited for exploring the intrinsic properties of the phosphide, including its cycling-induced capacity fade.

In this work, we prepared thin films of pure iron phosphides by an electrochemical deposition process, in an effort to develop model systems for evaluating iron phosphides as the anode in lithium secondary battery. For this purpose, iron phosphides with different phosphorus contents were obtained by controlling deposition conditions and the as-prepared electro-deposits were heat treated to obtain a desired crystallinity. The resulting samples were electrochemically analyzed using cyclic voltammetry, galvanostatic charge/discharge experiments, and electrochemical impedance spectroscopy.

In the presentation, the dependence of the Fe/P ratio on deposition conditions will be given. For the selected Fe/P ratios, the electrochemical responses from additive-free thin films and conventional powder-based composites will be comparatively analyzed. Moreover, the feasibility of the iron phosphide electro-deposits as the anode in lithium secondary battery will be discussed.

References

Y. U. Kim, C. K. Lee, H. J. Sohn, T. Kang, J. *Electrochem. Soc.*, **151**, 933 (2004)
M. Cruz, J. Morales, L. Sánchez, J. Santos-Peña, F. Martín, J. *Power Sources*, **171**, 870 (2007)