

Localized in-situ Study of Lithium-ion Transport in Graphene-based Electrodes by Scanning Probe Microscopy

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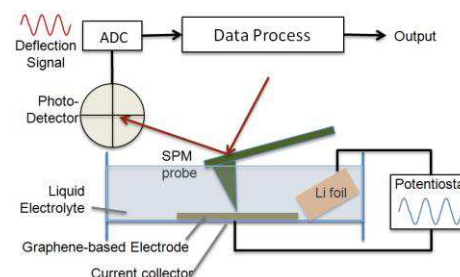


Fig.1. A simplified schematic diagram of the experimental setup

Until recently, most of Li-ion battery characterizations have relied on cyclic voltammograms and/or electrochemical impedance spectroscopy in a bulk-scale, where only cell-averaged quantities were available. However, these volume-averaged quantities limit fundamental understanding of solid electrolyte interface formation, ionic diffusion, and intercalation/de-intercalation process. Considering the charge transport and surface redox reaction occur at the nanoscale, direct nanoscale observation is essential for a more fundamental understanding on these phenomena.

Scanning probe microscopy is arguably the only tool capable of achieving true nanoscale while the in-situ condition of liquid electrolyte-based ionic cell is not disturbed. There have been several efforts to perform in-situ experiments in Li-ion battery using scanning probe microscopy (SPM), but they have been limited to the observation of morphological evolution of electrodes under various cell operation conditions.[1-3] Recently, Balke et al. presented a SPM-based observation on the nanoscale expansion of carbon electrodes by utilizing the fact that insertion of ions into the carbon materials dilates its volume.[4]

In this study, we present a SPM-based in-situ nanoscale electrochemical characterization on lithium-ion transport in graphene-based electrodes using a scheme similar to that of Balke et al.'s. The graphene-based electrodes include a reduced graphene oxide (RGO) and an RGO-MnO₂ nano-particle composition. Herein, scanning probe is used as the probe to track Li-ion transport during charge/discharge processes. The experimental setup is shown in Fig. 1. Surface elevation (i.e., cantilever deflection signal) is measured using the SPM tip to uncover localized variation of ionic transport behavior during charging/discharging processes between a Li foil and the graphene-based electrode in a liquid lithium hexafluorophosphate electrolyte. (Ionic transport causes a change in the surface morphology of the electrode as shown in Fig. 2.) Using the cantilever deflection signal in response to the charging cycles with various charging/discharging rates, we observe the variation in the amount of intercalated/de-intercalated species and the time constants of these intercalation/de-intercalation processes depending on the location of the probe on the graphene-based electrodes. Based upon the localized observations, we discuss the influence of defects and/or location of graphene layers (e.g., basal plane vs. edge at the layer steps) on the electrochemical activity, diffusion and other morphological/electrical evolutions.

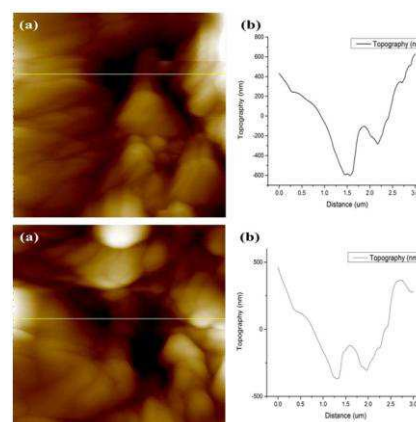


Fig.2. Morphological evolution of RGO-Mn₃O₄ electrode during a de-intercalation process

- [1] L. Y. Beaulieu, S. D. Beattie, T. D. Hatchard, and J. R. Dahn, *Journal of the Electrochemical Society* 150 (2003) A419.
- [2] F. P. Campana, R. Kotz, J. Vetter, P. Novak, and H. Siegenthaler, *Electrochemistry Communications* 7 (2005) 107.
- [3] J. Zhu, J. K. Feng, L. Lu, and K. Y. Zeng, *Journal of Power Sources* 197 (2012) 224.
- [4] T. M. Arruda, M. Heon, V. Presser, P. C. Hillesheim, S. Dai, Y. Gogotsi, S. V. Kalinin, and N. Balke, *Energy & Environmental Science* 6 (2013) 225.