

Imaging state of charge and its correlation to strong interaction variety in graphene based nano hybrid for energy application: a case study of LMFP-graphene

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To make lithium ion battery another successful revolution in automobile industry, its power performance has to be largely improved which is primarily limited by cathode materials. Graphene based nanohybrid, for instance graphene supported olivine $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$ nanorod (LMFP-graphene)¹, has been elevated into a star as a promised high energy and high power cathode. The unique structure (reduced pathway of Li^+ transportation and intimate bonding to high electronic conductor, graphene) in such hybrid contributes to overcome the intrinsic low Li^+ transportation speed in olivine structure. P-O-C bonding in such hybrid has been unambiguously confirmed by X-ray absorption near edge structure (XANES) spectroscopy at C and O K-edges. This interaction, as being evidenced by an increase of C=O absorption peak at 288.5 eV and being also observed in many carbon nanostructure based hybrids, not only anchors the nanorods onto the graphene but also modifies its surface chemistry for an enhanced Li^+ diffusion channel, both of which afford the nanorods-graphene hybrid ultrahigh-rate performance in lithium ion battery². The knowledge of such structure variation in individual hybrid particles is worth of investigation because of its potentially significant impact on the high rate performance. This can be tackled by studying the charge compensation, phase transformation along charging at the different state of charge (SOC). Therefore study of the local SOC distribution in a single LMFP nanostructure and correlation of this distribution with the interactive bonding variations shall be of great fundamental importance. Scanning transmission X-ray microscopy (STXM) using a focused beam size of ~25 nm provides an excellent combination of chemical/electronic structure speciation (XANES) and microscopic studies of various nanostructures including studies of the electronic structure and surface interaction of individual CNT or graphene supported catalyst³ as well as dopant distribution in a single N-doped CNT⁴ or structure variation within a single graphene⁵. This study reports an application of STXM in the chemical imaging of Fe valance distribution (equivalent to SOC distribution) in a single LMFP-graphene hybrid at Fe L-edge

since XANES study has proved that Fe is the redox center rather than Mn. Then the SOC distribution is correlated to the interaction strength represented by the C K-edge STXM XANES from the same LMFP-graphene. The results clearly approve our assumption of the spatial correlation between the stronger interaction and better charge performance. Such information will advance our understanding of the intrinsic relationship between structure and performance for LMFP-graphene in this case and can be globally extended to many different nanohybrids^{6,7}.

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