Emergence of a pre- π* Feature in Graphite upon Intercalation: An Experimental and Theoretical Study of Hexafluorophosphate

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Since 1841, graphite intercalated compounds (GICs) have been extensively studied leading to their use in thermal and electrical conductors, catalysis, and energy storage, particularly in lithium ion batteries (LIBs). Although LIBs are extensively used in applications such as mobile electronics, electric transportation, and grid storage, their transition-metal cathodes have a number of drawbacks related to cost, energy density and environmental impact, leading to a search for alternatives, such as a dual-carbon battery, in which both the cathode and anode are graphitic. In a graphite cathode, anions are intercalated during charging and deintercalated upon discharge.

PF_6-intercalated graphite, in particular, has several favorable properties such as a high storage capacity and discharge rate and a diffusivity similar to that of lithium in cathodes such as $LiFePO_4$ or $LiCoO_2$. Despite this, there are properties of this material that are controversial, particularly the intercalant layer spacing and staging at high potentials. How the electronic properties of PF_6 GICs are perturbed is understudied. In addition to these issues, which affect the use of this material in real devices, XANES spectra show a pre-π* feature, making this system also of fundamental theoretical interest. To clarify these issues, we study PF_6 intercalated graphite cells using techniques sensitive to the unoccupied partial density of states, X-ray Raman spectroscopy (XRS) and XANES, as well as X-ray emission spectroscopy, which is sensitive to the the occupied partial density of states. These spectra are interpreted using theoretical spectral calculated using density functional theory (DFT).

Excellent agreement with the XRS and XES spectra is obtained. A pre-π* feature in the XRS/XANES spectra, frequently seen in graphitic systems, is observed. We demonstrate that this feature is due to a transfer of charge from the host graphite lattice to the intercalated PF_6 molecules, which results in an overall lowering of the Fermi energy level. A comparison of the calculated structure with the XRD data suggests this material has a staging level of 2 when maximally intercalated.