

Exceptional Na-Ion Storage Mechanism in Hard Carbon : Critical Role of Micropores

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Utilization of hard carbon as an anode material in sodium ion batteries (SIBs) have received considerable attention in recent years. Many works on the potential of hard carbon has been carried out, but many hypotheses regarding Na⁺ ion storage mechanism appear to be debatable. It is not yet well known what are possible contribution of active sites (defect on surfaces, interlayer spacing between graphene sheets, and micropores)^[1] to the capacities in the sloping and plateau regions. In this paper, a series of hard carbon was prepared through pyrolysis of concentrated strong acid hydrolysis lignin (CSHAL) at various temperatures between 1000 and 1500 °C to investigate the active sites for Na⁺ ion uptake and electrochemical performance in the sloping and plateau regions. By using *ex-situ* small angle X-ray scattering, *ex-situ* X-ray diffraction, *ex-situ* XPS, electrochemical techniques, and the GITT method, we developed new mechanistic insights into the Na⁺ ion storage in the hard carbons. At the beginning of the sodiation process, Na ions could adsorb on the defect sites, followed by partial micropore filling in the sloping region. In the plateau region, intercalation of Na⁺ ions could occur at between graphene sheets, which ends with the micropore filling. On the other hand, during the initial step of desodiation process, complete stripping on micropore occurs first followed by deintercalation and desorption on defect sites. Moreover, the new Na⁺ ion storage mechanism reveals the role of micropore, which is key characteristic of hard carbon and the origin of hysteresis.

References:

[1] Bommier, C., et al., *New Mechanistic Insights on Na-Ion Storage in Nongraphitizable Carbon*. Nano Letters, 2015. **15**(9): p. 5888-5892.