

# Revisiting Lithium- and Sodium-Ion Storage in Hard Carbon Anodes

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The galvanostatic lithiation/sodiation voltage profiles of hard carbon anodes are simple, with a sloping drop followed by a plateau. However, a precise understanding of the corresponding redox sites and storage mechanisms is still elusive, which hinders further development in commercial applications. Here, a comprehensive comparison of the lithium- and sodium-ion storage behaviors of hard carbon is conducted, yielding the following key findings: 1) the sloping voltage section is presented by the lithium-ion intercalation in the graphitic lattices of hard carbons, whereas it mainly arises from the chemisorption of sodium ions on their inner surfaces constituting closed pores, even if the graphitic lattices are unoccupied; 2) the redox sites for the plateau capacities are the same as those for the closed pores regardless of the alkali ions; 3) the sodiation plateau capacities are mostly determined by the volume of the available closed pore, whereas the lithiation plateau capacities are primarily affected by the intercalation propensity; and 4) the intercalation preference and the plateau capacity have an inverse correlation. These findings from extensive characterizations and theoretical investigations provide a relatively clear elucidation of the electrochemical footprint of hard carbon anodes in relation to the redox mechanisms and storage sites for lithium and sodium ions, thereby providing a more rational design strategy for constructing better hard carbon anodes.

## 1. Introduction


Intercalation-based host materials that can store lithium ions in their crystallographic lattices have led to the commercial success of rechargeable lithium-ion batteries (LIBs).<sup>[1,2]</sup> The robust host structures provide them with high reversibilities and cycling stabilities, enabling omnidirectional market-share expansion and beginning a new industrial era.<sup>[1–3]</sup> Over the last decades, studies have been extensively carried out to optimize and discover advanced active materials with relatively high electrochemical performances.<sup>[4–6]</sup> Accordingly, active cathode materials have been significantly modified from the initial LiCoO<sub>2</sub> system to more advanced ternary mixture systems of transition metals (e.g., Co, Ni, and Mn), resulting in a substantial increase in reversible capacities and redox potentials.<sup>[4]</sup> By contrast, the original graphite-based intercalation compound anodes have maintained their dominance, which is mostly due to the absence of

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