

# Tracking Electrochemical (De)sodiation of Hard Carbon by Electrochemical Impedance and Raman spectroscopy

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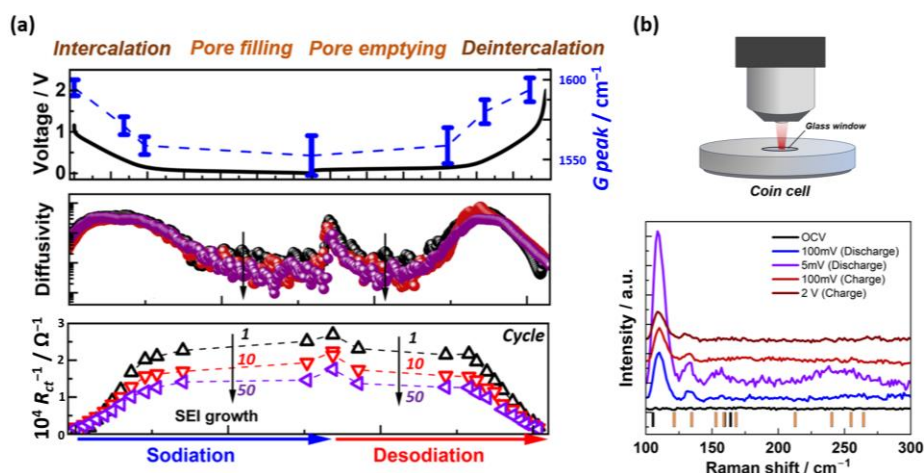
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Sodium-ion batteries (SIBs) are promising alternatives to lithium-ion batteries because sodium is more abundant and cost-effective when compared to lithium. SIBs require stable negative electrode material as graphite usually does not support sodium intercalation. Hard carbon, a highly disordered non-graphitizable material is a good option, having sodium storage specific capacity in the range of 200–480 mAh g<sup>-1</sup> below 1.2 V vs. Na<sup>+</sup>/Na.<sup>1,2</sup> Here, we thoroughly investigate the electrochemical (de)sodiation of hard carbon by means of electrochemical impedance spectroscopy (EIS), the galvanostatic intermittent titration technique, and *in situ* Raman spectroscopy for fresh and cycled electrodes. The results show G-band reversible shift and a strong change of the charge-transfer resistance above 0.1 V vs. Na<sup>+</sup>/Na indicating the intercalation of sodium ions into hard carbon, whereas the low-voltage plateau is associated with the pore filling process (Figure 1a). *In situ* Raman analysis demonstrates that the pore filling includes formation of small sodium clusters in closed pores (Figure 1b). As intercalation mechanism changes to pore filling at  $\approx$  0.10-0.15 V, apparent diffusivity decreases by an order of magnitude. The gradual growth of the solid-electrolyte interphase layer affects the rise of the interfacial resistance as cycling progresses. In combination with the slower diffusivity, the low-voltage plateau region strictly impedes fast de/sodiation and eventually causes capacity fade.



**Figure 1:** (a) Different stages of Na storage in hard carbon revealed by *in situ* Raman, GITT, and EIS, (b) *in situ* Raman spectra of hard carbon at low frequencies under different voltage.

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## References

1. J. Y. Hwang, S. T. Myung, Y. K. Sun, *Chem. Soc. Rev.* 2017, **46**, 3529
2. A. Kamiyama, K. Kubota, D. Igarashi, Y. Youn, Y. Tateyama, H. Ando, K. Gotoh, S. Komaba, *Angew. Chem. Int. Ed.* 2021, **60**, 5114.