

Elucidating functionalities of N-doped carbonaceous materials by means of in-situ TEM

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Background incl. aims

Nitrogen-doped carbonaceous materials gained broad interdisciplinary attention as low-cost, metal-free materials for photocatalysis, carbon capture, energy storage and water remediation. Their performance in real devices relies on the precise control of their nanostructure. Usually, nanostructural characterizations are done after completion of either the synthesis or the device operational cycle. Here we present two scientific questions related to functionalities of N-doped carbons, for which in-situ/in-operando TEM studies were crucial: (1) How N-doped carbons condensate from molecular precursors, and how can we thus guide their design as materials for CO₂-sorption¹ and (2) What is the nanoscale mechanism of Na storage in N-doped carbons when they are used as anodes in Na-batteries². The Methods and Results sections below are structured according to these two questions. Generalized conclusions on the application of the in-situ/in-operando methods to polymeric materials exemplified by N-doped carbons are given.

Methods

In this study we combined ex-situ high-resolution STEM, energy-filtered electron radial distribution function analysis, energy dispersive X-ray analysis and electron energy loss spectroscopy (at (1) different stages of condensation and (2) at different states of charge during electrochemical cycling) with in-situ STEM investigations: (1) in-situ heating was performed using a heating/biasing Protochips Fusion Select holder; (2) an in-operando Na half-battery was constructed using a Protochips Poseidon holder. 1 M solution of NaPF₆ in ethylene carbonate and diethyl carbonate was used as electrolyte.

Results

(1) By combining in situ condensation inside a STEM and ex situ analysis of the products of condensation at different temperatures and atmospheres, we were able to follow the structural, morphological, and chemical evolution of the uric acid and guanine precursors on the nanoscale upon heating and correlate it with the sorption properties of the obtained materials. We showed how one can control and tune the formation of pores in nitrogen-containing carbonaceous materials by varying pressures and reaction rates. We found that these two parameters change how the porosity of the surface develops, forming particles with mesopores (in vacuum) or microporous (in nitrogen) surfaces. Since this process co-occurs with cross-linking, the porous structure of the surface governs the subsequent release of volatiles and the development of the hierarchical pore structure. These findings allow us to synthesize N-doped carbons with a 2-times higher CO₂ uptake, keeping the same selectivity. (2) N-doped porous hollow carbon spheres (N-PHCs), which due to their size and shape, serve as an ideal model system to investigate Na-storage at the nanoscale, have been synthesized. By combining the ex-situ characterization at different states of charge with in-operando TEM experiments we found that at the beginning of sodiation a solvated ionic layer forms on the surface of N-PHCs, followed by irreversible shell expansion due to the solid electrolyte interface formation and subsequent storage of Na(0) within the porous carbon shell. We showed that binding between Na(0) and C creates a Schottky junction making Na deposition inside the spheres more energetically favorable at low current densities. During sodiation, the solid electrolyte interface fills the gap between N-PHCs, binding spheres together and facilitating the Na ions' transport in the direction of the current collector and

subsequent plating underneath the electrode. The N-PHCSs layer acts as a protective layer between the electrolyte and the current collector, suppressing possible growth of dendrites at the anode.

Conclusion

In situ/in-operando characterization, setups have been successfully applied to the characterization of N-doped carbonaceous materials. However, special attention is required for separating the electron-beam-induced effects and the processes we are interested in. The synergetic combination between ex-situ and in-situ experiments is crucial for obtaining realistic models of the studied processes.

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Keywords:

N-doped carbons, in-situ microscopy, batteries

Reference:

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