

In situ chemical imaging of H⁺ and hydrated Li⁺ ion intercalation in individual few-layered Ti₃C₂T_x MXene flakes

Namrata Sharma, Peer Bärmann, Louis Godeffroy, Faidra Amargianou, Andreas Weisser, Mailis Lounasvuori, Zoe Dessoliers, Markus Weigand, Tristan Petit

Young Investigator Group Nanoscale Solid-Liquid Interfaces, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Albert-Einstein Str. 15, 12489 Berlin, Germany

Recently, 2D transition metal carbides and nitrides, so-called MXenes, have emerged as a promising candidate for energy storage applications.¹ MXenes possess a unique combination of layered structure, surface functionality, nanosized interlayer spacing, and a conductive core that can be finely tuned.² Their charge storage mechanism varies depending on the electrolyte, incorporating electrostatic interactions, Faradaic reactions, or a combination of both. In aqueous electrolytes, their charge storage mechanism differs based on the charge carriers. The current consensus on Ti₃C₂T_x in aqueous neutral electrolytes suggests competing contributions from electrical double-layer (EDL) and pseudocapacitive charge storage, driven by the strong interaction between inserted cations and water solvent molecules within confined spaces.³ However, in acidic electrolyte, the charge storage is primarily attributed to redox pseudocapacitance via fast electrochemical (de)protonation of the oxygenated surface terminations.⁴ Previous studies have focused on macroscale electrodes, where the intrinsic ion-host interaction mechanism within individual pristine MXene flakes remains inaccessible due to the non-uniform stacking of MXene sheets. Local inhomogeneity of the ion intercalation in individual MXene flakes remain relatively unexplored experimentally.

Here, we employ in-situ STXM to investigate the local chemical changes within single Ti₃C₂T_x MXene flakes upon spontaneous and electrochemical (de)intercalation mechanism of Li⁺ cations and H⁺ in aqueous electrolytes. The sub-100 nm spatial resolution and the high chemical sensitivity at the Ti-L edge XAS enable mapping of the titanium oxidation state from the flake edges to its basal plane. Our findings reveal that Ti atoms in Ti₃C₂T_x MXenes undergo oxidation upon Li⁺ intercalation, and reduction upon H⁺ intercalation, challenging the current molecular picture of pseudocapacitive charging in Ti₃C₂T_x MXene in aqueous electrolyte. Furthermore, we explore the influence of flake thickness on Li⁺ ion and H⁺ intercalation mechanism. This study provides novel insights into the fundamental mechanism underlying pseudocapacitive charging in Ti₃C₂T_x MXene flake in both acidic and neutral electrolytes conditions, offering a refined understanding of charge storage processes at the single flake level.

References

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