Controlling the MAX-to-MXene Transition:

The Role of Electrochemical Etching

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Electrochemical etching of MAX phases is increasingly considered a promising and safer alternative to conventional MXene synthesis routes relying on concentrated HF, yet recent studies clearly indicate that this approach still requires substantial optimization to deliver materials with well-controlled and reproducible structures. Reported protocols often struggle with incomplete removal of the A layer, the concurrent formation of carbide-derived carbon, and a narrow processing window between selective etching and destructive oxidation of the $M_{n+1}X_n$ backbone.

In our setup, a glassy carbon crucible acts as the working electrode, a glassy carbon rod serves as the counter electrode, and an Ag/AgCl/0.1 M KCl electrode is used as the reference. The MAX phase is electrochemically etched in an aqueous electrolyte containing tetramethylammonium tetrafluoroborate dissolved in sulfuric or phosphoric acid, which provides a fluorine-containing anion without the use of bulk HF solutions and allows tuning of the proton activity and ionic strength. The process is performed for 48 h at a constant potential of 2 V versus Ag/AgCl, enabling a gradual weakening and removal of the A-layer while maintaining a well-defined electrochemical driving force. This controlled potential regime is intended to minimize uncontrolled corrosion and over-oxidation that frequently accompany purely galvanostatic or two-electrode configurations.

Scanning electron microscopy reveals the formation of layered, accordion-like morphologies characteristic of MXenes, with expanded interparticle gaps indicative of successful interlayer opening. Raman spectra exhibit bands typical of MXene phases, confirming preservation of the $M_{n+1}X_n$ framework and substantial removal of the A element from the parent MAX phase. At the same time, the extended etching time and relatively high anodic potential promote defect generation and local over-oxidation, which we highlight as an intrinsic limitation of the current protocol and a key target for further optimization.

By juxtaposing our results with the existing electrochemical etching literature, we discuss the main advantages (HF-free operation, potential tunability, access to diverse surface terminations) and drawbacks (possible defect-rich products, competing side reactions, sensitivity to electrolyte composition) of this route toward “greener” MXene synthesis. We argue that a carefully designed three-electrode configuration with a glassy-carbon working vessel provides a convenient platform to systematically map the etching window in terms of potential, time, and electrolyte chemistry, and thus to rationally tailor electrochemical protocols that can realistically compete with HF-based methods in terms of safety, scalability, and MXene quality.

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Acknowledgement:

This work was financially supported by the National Science Centre (Poland) via M-ERA.NET grant no.: 2024/06/Y/ST11/00223