MXing Electrochemical Hydrogen Evolution with MXenes

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Since the advent of the Industrial Revolution, non-renewable sources of energy, such as coal, oil, and natural gas, have served as the pillars of the energy supply for over a century. However, the exhaustion of fossil fuels came at significant environmental costs. From the transition of the last century to this century, there has been a growing demand for renewable clean sources of energy that offer sustainable alternatives. Hydrogen, one of the promising solutions, is a clean energy carrier that can be produced from various renewable sources. The advantage of Hydrogen lies in its high gravimetric density, and the only combustion by-product is water. Hence, with the progress of technology and the growth of energy demand, hydrogen is one of the best potential candidates to provide us with a sustainable energy future.

The best and most efficient approach to generating hydrogen is electrochemical water splitting, where we obtain hydrogen from the cathode side (**Figure 1a**). The disadvantage of the electrochemical hydrogen evolution reaction (HER) is the sluggish kinetics. To get rid of this shortcoming, significant research has been devoted to the development of electrocatalysts.[1] To date, the state-of-the-art catalyst is Platinum for HER which has its limitations of sparsity and cost-ineffectiveness. Hence, various strategies have been implemented to develop alternative cost-effective sources for efficient HER. Among them, one of the effective strategies has been to use 2D materials, both bare and in metal-incorporated 2D material fashion.[2] One of the most significant and recent discoveries made in this field is MXenes in 2011, named to emphasize its graphene-like morphology.[3]

MXenes are synthesized through a top-down synthesis approach from its precursor MAX phase, a group of layered, hexagonal ternary carbides or nitrides. Various procedures have been
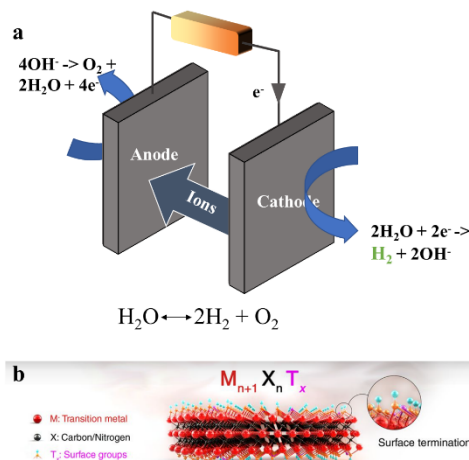

Figure 1. (a) Electrochemical water splitting showing hydrogen evolution reaction on the cathode side. (b) 2D MXene illustration showing the general formula and arrangement of elements in the lattice structure. Reproduced from ref 4.

established for the selective etching of the A-layer atoms (e.g., Al, Si, Ga) from the MAX phase to give rise to MXenes with a general formula of $M_{n+1}X_nT_x$ (**Figure 1b**), where M represents a transition metal site, X represents carbon or nitrogen sites (n varies from 1-4). T_x indicates surface termination groups (x is variable).[3,4] The immense potential of tunability of MXene structures gives rise to MXene applications starting from Electrochemical catalysis and energy storage to biomedicine.
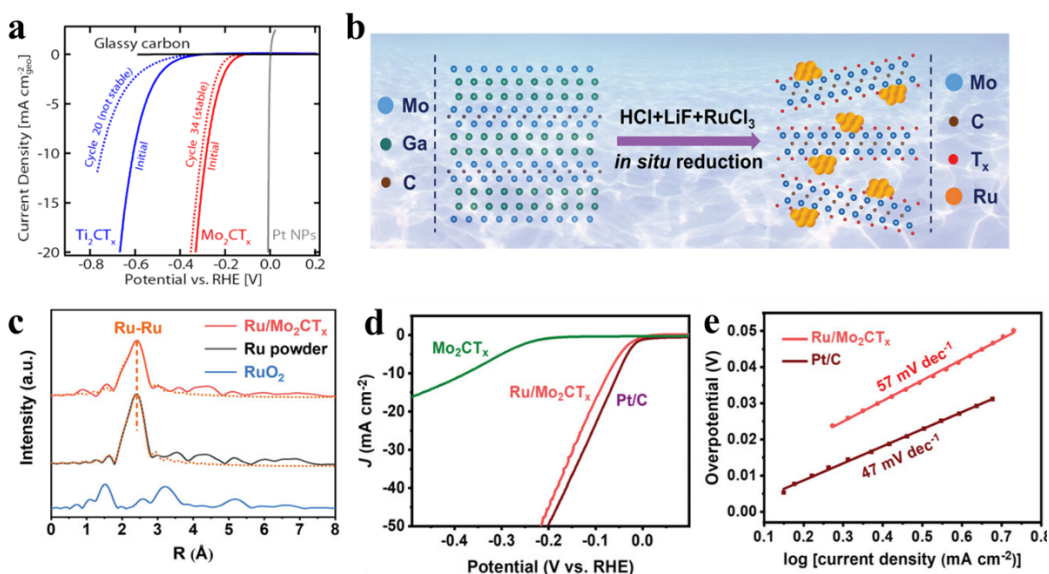

Figure 2 (a) LSVs (scan rate of 10 mV s^{-1}) of Mo_2CT_x, Ti_2CT_x, (Pt nanoparticles, and bare glassy carbon for comparison). Reproduced from ref 5. (b) Synthesis scheme for Ru/Mo_2CT_x MXene with RuCl$_3$ salt for Ru incorporation. (c) FT-EXAFS (solid lines) and best theoretical fits (dotted lines) of Ru/Mo_2CT_x, Ru powder, and RuO$_2$. (d) LSVs (scan rate of 5 mV s^{-1}), (e) Tafel plots of Ru/Mo_2CT_x (Mo_2CT_x and Pt/C shown for comparison). Reproduced from ref 6.

Seh *et. al.* showed that MXenes can be used as electrocatalysts for HER using theoretical calculations.[5] Subsequently, they synthesized the two best catalysts proven from theory, Mo_2CT_x, and Ti_2CT_x, and characterized their electrochemical performance (**Figure 2a**) in an acidic medium. The basal planes were established as the catalytically active sites with Mo_2CT_x being a superior catalyst to Ti_2CT_x. Although the performances were not at par with commercial catalysts, this was the first time MXenes were applied in the field of electrocatalysis. The low performance of bare MXenes predicted that MXenes can also be used as catalytic supports with metal catalysts incorporated into the lattice.

Electrochemical water splitting is generally preferable in either acidic or basic medium because of lower conductivity and proton supply resulting in higher mass transfer compared to neutral media. However, the extreme pH conditions lead to degradation effects in the electrochemical system. Ru clusters incorporated in

Mo_2CT_x MXenes (Ru/Mo_2CT_x) have shown increased HER in neutral medium.[6] The synthesis of these MXenes was done by the normal etching method (HCl and LiF) with $RuCl_3$ salt (**Figure 2b**). The Fourier transform of extended X-ray absorption fine structure spectroscopy (FT-EXAFS) fitting showed lower coordination for the Ru/Mo_2CT_x in comparison to metallic Ru confirming abundant exposed surface atoms to exhibit enhanced catalytic activity (**Figure 2c**). The η_{10} (overpotential at the current density (j) of 10 mA cm^{-2}) of 73mV and the Tafel slope (ratio of the overpotential and log{j/j_0} where j_0 is the exchange current density) of 57 mV dec^{-1} is at par with commercial Pt/C catalysts (**Figure 2c, d**). This study leaves us with the question of having other cost-effective metals with different MXenes.

Sun *et. al.* shows a strategy for lattice engineering of $Ti_3C_2T_x$ MXene nanosheets for optimal Pd anchoring which results in increased HER activity (**Figure 3a**).[7] The authors used a simple synthesis method to introduce alkali metal cations (A = H^+, Na^+, Li^+, K^+ - structures named as PdAMX). The increased interlayer distance and disordered structure are shown from the XRD patterns of the samples. Pd was subsequently incorporated into the sample, with the K^+ showing the most optimal incorporation (PdKMX). A comparative study of the electrochemical performances of different structures showed the maximum efficiency of the PdKMX structure.
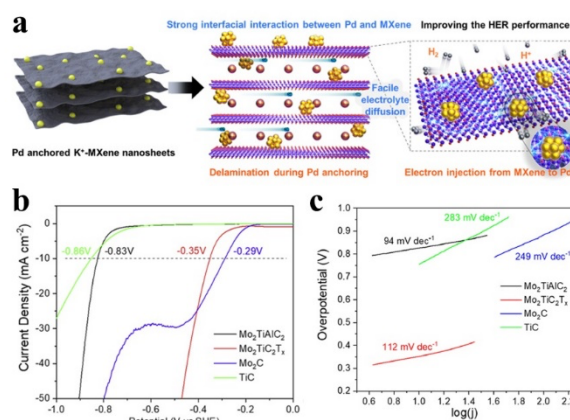

Figure 3 (a) Schematic showing formation steps of Pd anchored MXene. Reproduced from ref 7. (b) LSVs (scan rate of 10 mV s^{-1}) and (c) Tafel slope of Mo_2TiAlC_2 (MAX) and $Mo_2TiC_2T_x$ (MXene) along with other phases showing competition between two phases for HER. Reproduced from ref 8.

MXenes can have two metals in the M sites of their unit cell, known as solid solution MXenes which can also show HER. Luxa *et. al.* recently showed HER activity dependency with compositional transformation in Mo_2TiAlC_2 MAX to its derivative $Mo_2TiC_2T_x$ MXene phase. Characterization methods such as XRD, and XPS showed a well-separated phase formation of the two phases which contribute to the HER activity. The performance plots of the two phases show that the MXene phase has a lower η_{10} (higher activity) (**Figure 3b**) whereas the MAX phase shows a smaller Tafel slope (**Figure 3c**) suggesting faster electron transfer kinetics. The interesting fact proven here is how different phases can compete for activity and kinetics which are important parameters for HER.

The works shown above show different directions in which MXene-based HER catalysts can propagate. The high scalability and the chemical tunability in the MXenes make it a promising candidate for 2D HER catalysts at par with commercially established ones. The clean future holds great promise for MXenes being both fuel-generating and storage material.

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