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Review Article

Theoretical modelling of the Hydrogen evolution reaction on MXenes: A critical review

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Abstract

MXenes, two-dimensional (2D) transition-metal carbides and nitrides with diverse compositions and structures, have attracted notable attention due to their potential as promising alternatives to the conventional Pt-group catalysts for the hydrogen evolution reaction (HER). Hereby, we analyze the state-of-art approaches in theoretical modelling HER in MXenes with the aim of assessing their intrinsic activity for this crucial electrocatalytic reaction, analyze diverse thermodynamic and electronic properties proposed as descriptors, inspect kinetic aspects, and explore linear scaling relations. Ultimately, we present an overview of the challenges, perspectives, and future research of HER in MXenes.

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Introduction

The rising energy demand and depletion of natural resources require renewable energy sources [1–3]. Molecular hydrogen (H_2) shows promise as an alternative fuel [4–6]. Current industrial hydrogen production has limitations [7,8], but electrochemical processes offer a sustainable solution. Efficient and cost-effective electrocatalysts are vital for widespread use [9,10]. Two-dimensional (2D) materials, MXenes, have shown promising potential as HER electrocatalysts [11–19]. These materials exhibit a chemical formula of $M_{n+1}X_nT_x$ with $n = 1–4$, M is an early transition metal, X stands for carbon and/or nitrogen, and T_x are terminating functional groups such as O, H, OH, or F (*cf.* Figure 1a–b) [17]. MXenes are obtained from chemical etching of A elements from a MAX phase precursor using F-containing etchants like hydrofluoric acid (HF), either directly [17] or *in situ* [20*]. Surface termination can be controlled [21], and F-free synthesis [22] methods are available. Some treatments yield clean MXenes [23], allowing for adjustments in composition, thickness, and surface termination. This concise review explores MXene's HER using computational methods, discussing reaction mechanisms, activity descriptors, and future research trends.

Hydrogen evolution reaction and MXene electrocatalysts

The general mechanisms of the HER were established for most materials including MXenes [24–33]. Two possible well-agreed mechanisms for the HER reaction, Volmer-Heyrovsky and Volmer–Tafel (*cf.* Figure 1c) [25]. Both share a first electrochemical step as is Eq. (1).

$$\text{Volmer step: } H^+ + e^- + * \rightarrow H^* \quad (1)$$

where * represents an active site and H* represents an adsorbed hydrogen atom. These two mechanisms differ on the second step, represented in Eqs. (2) and (3).

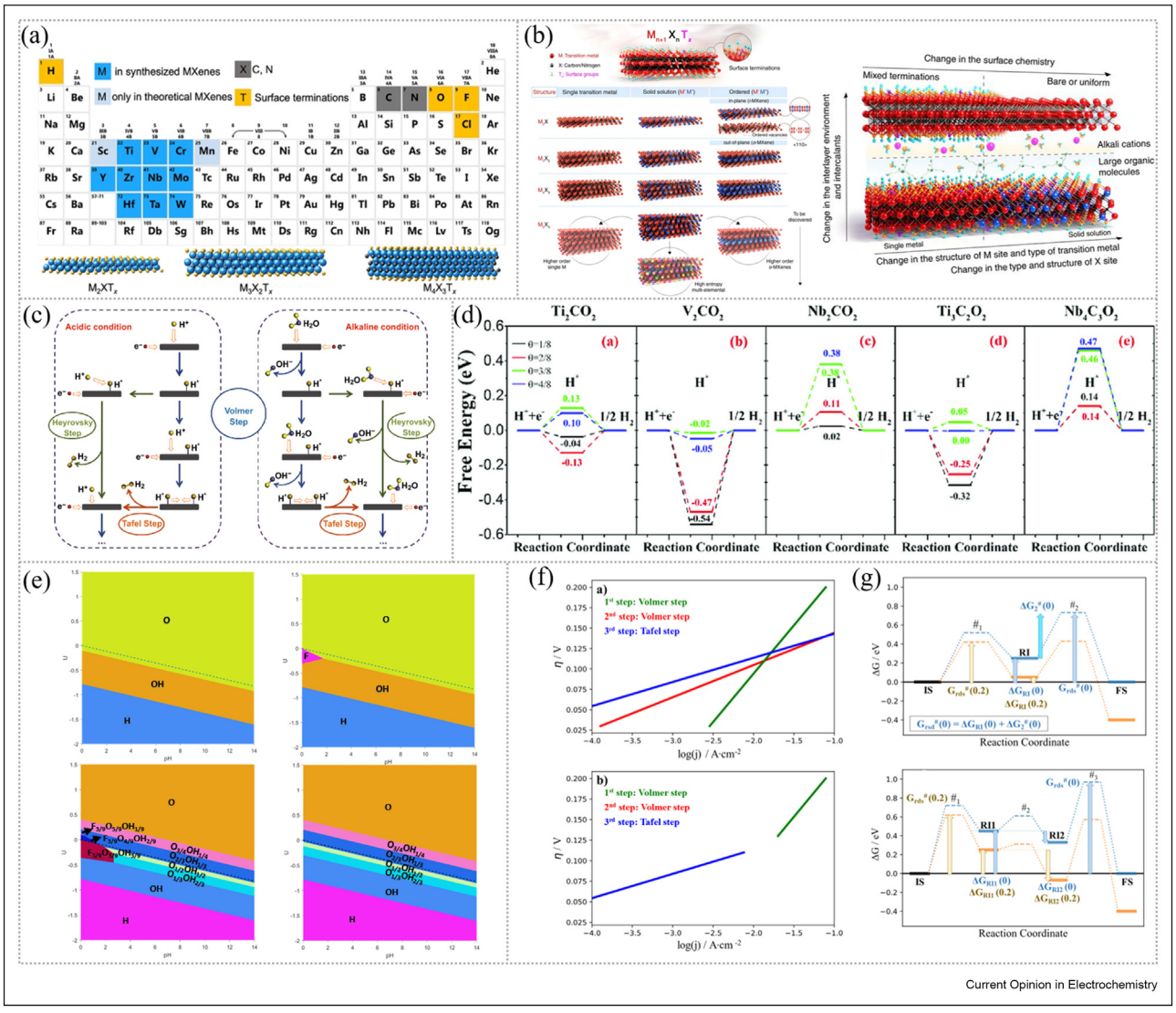
$$\text{Heyrovsky step: } H^+ + e^- + H^* \rightarrow * + H_2 \quad (2)$$

$$\text{Tafel step: } 2H^* \rightarrow * + H_2 \quad (3)$$

The Heyrovsky step is electrochemical nature, whereas Tafel step involves the recombination of two previously reduced protons.

Meng et al. [26*] found that the reaction could potentially start from H atoms of –OH or –H terminations, besides the reduction of aqueous H^+ in VH or VT mechanisms. They also explored the termination effect on HER mechanism of Ti_3C_2 MXene, pointing out that models featuring mixed terminations lead closer to the HER equilibrium line with thermodynamic overpotential of 0.01. All in all, MXenes showed outstanding performance as HER electrocatalysts [34,35] and several descriptors have been proposed to evaluate their HER electrocatalytic properties [36*,37*].

Figure 1



(**a**) All elements involved in different MAX phases. Reprinted with permission from Ref. [73]. (**b**) Schematic illustration of the MXene structures with $M_{n+1}X_nT_x$ general formula (see text), reprinted with permission from ref. [20]. (**c**) Schematic Volmer-Heyrovsky and Volmer–Tafel pathways for hydrogen evolution reaction (HER) under acidic and alkaline conditions. Reprinted with permission from ref. [24]. (**d**) Free energy diagram of HER processing on Ti_2CO_2, V_2CO_2, Nb_2CO_2, $Ti_3C_2O_2$, and $Nb_4C_3O_2$ under standard conditions. Reprinted with permission from ref. [65]. (e) Pourbaix diagrams for Ti_3C_2 MXene (0001) surface regarding fully −O, −OH, and −H terminated surfaces (left), or including as well fully −F terminated surfaces (right). Reprinted with permission from ref. [26]. (f–g) Schematic representation of an arbitrarily chosen Gibbs free energy profile and linear Tafel regimes based on the V_2C–H model for the Volmer-Heyrovsky and Volmer–Tafel mechanisms. Reprinted with permission from ref. [50].

Thermodynamic approach to the HER by MXenes

The calculated Gibbs free energy (ΔG) of HER intermediates is crucial for assessing the activity of electrocatalysts like MXenes as it is directly related to the potential determining step (PDS). For the equilibrium in Eq. (4) at 1 bar and 298.15 K

$$H^+_{(aq)} + e^- \leftrightarrow 1/2 \cdot H_2(g) \quad (4)$$

the computational hydrogen electrode (CHE) model, [38] allows one to estimate the chemical potential of the left-hand side and to relate it to the standard hydrogen

electrode (SHE), which takes the potential for Eq. (4) as zero. In the case of MXenes, one has

$$\Delta G_H = \Delta E_H + \Delta E_{ZPE} - T\cdot\Delta S_H, \quad (5)$$

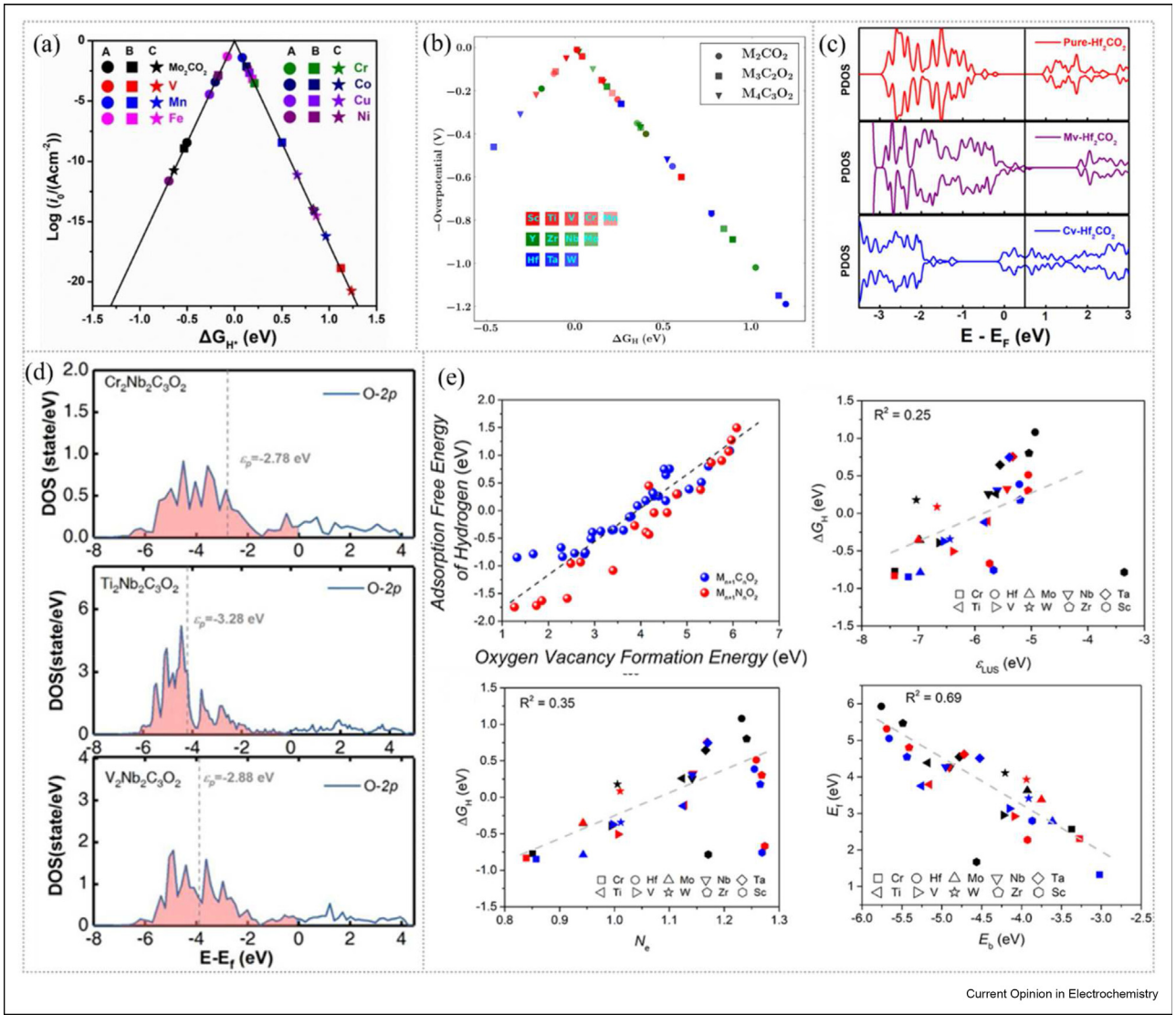
and

$$\Delta E_H = E_{nH/MXene} - E_{(n-1)H/MXene} - 1/2\cdot E_{H_2} \quad (6)$$

where $E_{n\mathrm{H/MXene}}$ and $E_{(n\text{-}1)\mathrm{H/MXene}}$ are the total energy of the MXene model with *n* and *n-1* H adatoms, respectively, E_{H_2} is the H_2 molecule energy in vacuum, the ΔE_{ZPE} and ΔS_H terms account for the difference in zero-point-energy contribution and entropy change, respectively. A variant of this descriptor has been proposed [39*,40*], that is directly related to the rate determining step (RDS) although not widely used yet (*cf.* Figure 1d).

In MXenes, the −O termination [41] is the primary active site for H adatom. However, analyzing other potential active sites requires further investigation. Here, ΔG_H appear to be a key descriptor for HER catalyzed by MXenes [42], consistent with the *Sabatier* principle. Optimal H adsorption strength is vital for efficient reaction rates at different steps. However, while the ΔG_H maximum corresponds to the HER PDS,

Figure 2



(**a**) The volcano curve of exchange current (i_0) as a function of the ΔG_{H^*}. Reprinted with permission from ref. [63]. (**b**) Negative of the overpotential of MXenes plotted versus ΔG_{H^*}. Reprinted with permission from ref. [28]. (**c**) Projected density of states (PDOS) of the O atom on Hf_2CO_2 with different vacancy types. Reprinted with permission from ref. [47]. (**d**) DOS plot of $Cr_2Nb_2C_3O_2$, $Ti_2Nb_2C_3O_2$, and $V_2Nb_2C_3O_2$. The ε_p values denote the position of O-2*p* band center with respect to the Fermi level. Reprinted with permission from ref. [32]. (**e**) Linear relationship between ΔG_{H^*} and oxygen formation energy (E_f), the lowest unoccupied state (ε_{LUS}), number of electrons gained by oxygen atom (N_e) and oxygen binding energy (E_b). Reprinted with permission from ref. [37].

Brønsted–Evans–Polanyi (BEP) relationships [43,44] justify considering it as RDS. However, more researches are required to investigate the kinetics and determine the true RDS in the HER process. Using $\Delta G_H = 0$ as a design criterion is controversial because it assumes equilibrium conditions without considering overpotential or non-thermoneutral conditions [45,46]. Additionally, there are several computationally based proposals to improve the MXenes HER through structural modifications [29,30,33,47,48].

Pourbaix diagrams are useful for determining the surface composition of an electrode under specific pH and potential conditions using the CHE method [38]. Analyzing Pourbaix diagrams is an essential step in computational studies. While previous works on MXenes primarily focused on the stable –O termination (*cf.* Figure 1d) [41], this may not be the most stable under electrochemical conditions. More recently, Meng et al. [26*] and López et al. [27*] considered Pourbaix diagrams for MXenes involving several terminations (*cf.* Figure 1e). Ashton et al. [49] used them to predict favorable MXene synthesis conditions.

Kinetic aspects of HER by MXenes

Studying the transition states (TSs) for the VH and VT mechanisms in HER is complex due to coupled proton-electron transfers. Some studies treated them as non-electrochemical steps. Only one study by López et al. [50*] investigated the kinetics of HER on V_2C MXene (*cf.* Figure 1f–g) and simulated the Tafel slope, which indicates the reaction rate based on current density and overpotential [31,51,52]. The Tafel also is provided about the rate from the current density (j) and as in Eq. (7) [53],

$$\log_{10} j\ (\eta) = \log_{10} j_0 + \eta/b, \tag{7}$$

where $1/b$ is the Tafel slop, j and j_0 are the current density and exchange current density, respectively [54]. The relationship between the free energy landscape and the Tafel plot is complex. Accurate measurements require quasi-equilibrium [55,56] or steady-state [57] conditions. Tafel slopes are condition-specific and influenced by several factors [58–61]. Furthermore, the role of the frequency factor (A) in MXenes HER activity also should be explored, as it is known that HER activity of noble metals involves high A values [62].

Descriptors of the Hydrogen evolution reaction by MXene electrocatalysts

Various descriptors have been proposed to evaluate the HER performance of MXenes, including the HER overpotential (η) [28], the exchange current j_0 [63], as in Eq. (7), and ΔG [64], being used to represent MXenes catalytic activity and identify important properties through volcano plots (*cf.* Fig. 2a and b). Among them, especially the d-band (ε_d) and p-band (ε_p) centers, are often used as descriptors for HER activity [65–67] (*cf.* Figure 2c and d). Anand et al. [67] suggested that a closer ε_d to the Fermi level improves charge transfer kinetics. Jin et al. [32] found a correlation between ε_p and ΔG_H, indicating the impact of the outer metal layer on HER activity and H adsorption. Further details can be found in Fig. 2e and summarized in Table 1. Exploring the linear relationship between descriptors is crucial for evaluating HER activity. It can reduce the cost of high throughput screening and facilitate the synthesis of MXenes with enhanced HER activity based on theoretical principles.

Table 1

Overview of potential linear relations for HER on MXenes proposed in recent years. These involve various properties such as Bond Length (BL), the Bader charge variation (N_e), Gibbs free energy of hydrogen adsorption (ΔG_H), binding and formation energy of modified MXenes (E_b and E_f), Fermi level energy (E_{Fermi}), the lowest unoccupied state (ε_{LUS}), the highest peak position (E_p), p-band centre (ε_p) of density of state (DOS), overpotential (η), exchange current (j_0), the number of valence electrons, atom radius, and electronegativity of doped atoms of MXenes. The corresponding references are also indicated.

Relevance	BL	N_e	ΔG_H	E_b	E_f	E_{fermi}	*Ref.*
BL		√	√			√	[32,33,36*]
N_e	√		√	√	√		[33,36*,37*]
ΔG_H	√	√		√	√		[32,36*,37*]
E_b		√	√		√		[29,37*]
E_f		√	√	√			[29,37*]
E_{Fermi}	√						[37*]
ε_{LUS}			√				[37*]
E_p/ε_p			√				[32,47]
η							[28]
j_0							[63]
H-coverage	√	√	√				[30,65,71]
Atom Radius	√			√			[72*]
Valence Electron Num.			√				[72*]
Electronegativity			√				[72*]

Summary and outlook

MXenes are promising candidates as efficient electrocatalysts for hydrogen production. Screening MXenes through experiments or modeling using grounded descriptors simplifies evaluation and design. However, a comprehensive overview of recent developments and expanded descriptors is missing. Further research is needed to explore the role of mixed surface terminations under realistic conditions, as most studies have focused on specific terminations. Also, advanced approaches, like explicit inclusion of solvation effects [68] and making used grand-canonical DFT [69], reshape the understanding of electron transfer reactions and catalytic activity on MXene materials. HER kinetics and appropriate modeling with descriptors have received limited attention. Further exploration is needed in this

area. Additionally, machine learning [70*] is widely used to accelerate the discovery and design of catalytic materials, but its development is ongoing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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