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Short Communication

Electrocatalytic activity of layered MAX phases for the hydrogen evolution reaction

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ABSTRACT

The hydrogen evolution reaction (HER) is important for the advancement of next-generation electrochemical energy devices. The search for an alternative inexpensive catalyst for energy conversion to replace expensive and rare noble metals is of high priority. There has been a significant push to investigate electrocatalysis of various layered materials for hydrogen evolution. However, the electrocatalytic activity of layered MAX phases remains largely unexplored. Herein, electrocatalytic activity studies of MAX (Ti_2AlC, Ta_2AlC, Ti_2SnC, Ti_3SiC_2, V_2AlC, Mo_2TiAlC_2, and Cr_2AlC) phases are conducted. Material and electrochemical characterization are carried out to understand the morphology and catalytic activity, respectively. From Tafel slope analysis, it was found that proton adsorption is the rate-limiting step for all the MAX phases studied. Double transition-metal MAX carbides (Mo_2TiAlC_2) showed better catalytic activity for HER than single transition-metal MAX carbides.

1. Introduction

Exploring clean, renewable, and efficient strategies for energy production is a major challenge in the present situation. Natural resources are being depleted at an alarming rate and the use of sustainable energy sources is encouraged [1–4]. Among the available sustainable energy sources, electrochemical energy is an ideal and efficient method to address the present energy crisis. Hydrogen energy is attracting immense attention due to its zero carbon emission and high energy density [5]. Electrochemical splitting of water to generate hydrogen via the hydrogen evolution reaction (HER) is an ideal step towards efficient electrocatalysis [3,6–8]. Noble metal catalysts such as platinum are considered to be the most efficient catalysts for HER, but face major disadvantages for large-scale hydrogen production due to their scarcity, and high cost [9]. Thus, dependence on expensive noble metals has been significantly reduced while the use of alternative inexpensive catalysts has been encouraged [3,10].

In addition, a number of two-dimensional (2D) materials such as graphene [11,12], transition metal dichalcogenides (TMDs) [13-16], transition metal phosphides [17,18], and heavy pnictogens [19] such as As, Sb, and Bi have been shown to be promising electrocatalysts. Although 2D nanomaterials have been extensively used for energy conversion applications, some have faced a setback due to their poor intrinsic activity, low density of active sites, or weak conductivity [20]. These nanomaterials have been tuned to improve their properties for fast catalytic reaction kinetics. Beyond this, there is another class of layered materials known as MAX phases that remain largely unexplored for hydrogen evolution applications.

About 150 MAX phases are known and the family continues to expand [21,22]. MAX phases are layered carbides and nitrides with the general formula $M_{n+1}AX_n$ where $n = 1–3$, M represents an early transition metal, A is an element of group 13–14 and X is carbon or nitrogen [23-25]. Studies have also shown the successful synthesis of $(M', M'')_{n+1}AlC_n$ ordered phases, where two M' layers sandwich one or two M'' layers [26,27]. MAX phases show the properties of both ceramics and metals due to their layered structure and the intrinsic nature of their

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chemical bonding. They exhibit good electrical and thermal conductivity, have a high elastic modulus, thermal shock resistance, damage tolerance, are readily machinable, and resistant to both oxidation and corrosion [21,28–31]. The bonding of layers in MAX phases is stronger and requires a stronger etching and exfoliation method to convert them to another set of interesting materials called MXenes [32,33]. They are presently a hot topic in the scientific community and in industry due to their energy-related applications [1,34–36].

We have studied the electrocatalytic activity of a set of MAX phases for their possible energy conversion applications as these have not yet been investigated. Morphological studies were carried out using a scanning electron microscopy (SEM) and the elemental composition was confirmed from EDX spectra. The distribution of constituent elements was analyzed using EDX mapping. Linear sweep voltammetry (LSV) was carried out to study the catalytic properties of the material towards HER. Herein, we add new candidates to the existing list of known layered materials for electrochemical and electrocatalytic applications.

2. Experimental section

2.1. Materials and characterization

MAX phases (Ti_2AlC, Ta_2AlC, Ti_2SnC, Ti_3SiC_2, V_2AlC, Mo_2TiAlC_2, and Cr_2AlC) were purchased from Laizhou Kai Kai Ceramic Materials Co., Ltd, China. Sulfuric acid (H_2SO_4) of analytical grade, isopropanol, and Nafion were procured from Sigma Aldrich, Germany. The surface morphology of the MAX phases was observed using a scanning electron microscopy (SEM, TESCAN LYRA 3). The elemental analysis and mapping were carried out with an energy-dispersive X-ray (EDX) detector (BRUKER XFlash 5010) within the SEM.

2.2. Electrochemical measurements

MAX phases (5 mg mL^{-1}) were dispersed in a solution containing isopropanol and distilled water in a ratio of 3:2, respectively. 40 μL of Nafion binder was added to the mixture. Prior to drop-casting the mixture over glassy carbon (GC), the mixture was subjected to ultrasonication for 60 min to obtain a well-dispersed suspension. 10 μL of the suspension was then drop-casted over GC electrode and left to dry at room temperature. Voltammetry measurements were conducted using a potentiostat (PGSTAT 204, Metrohm Auto lab) operated by Nova 2.14 software. The hydrogen evolution reaction (HER) was investigated by linear sweep voltammetry (LSV) at a scan rate of 5 mV s^{-1} in 0.5 M H_2SO_4. The measurements were carried out at room temperature with Ag/AgCl (1 M KCl) as the reference electrode (RE) and platinum wire as the counter electrode (CE). The reference electrode was calibrated versus the reversible hydrogen electrode (RHE), where $E_{RHE} = E_{Ag/AgCl} + E^0_{Ag/AgCl} + 0.059 \times pH$. Chronoamperometry measurements were carried out using a rotating disk electrode (RDE) in 0.5 M H_2SO_4 solution.

3. Results and discussion

The morphology of the MAX phases was analyzed using a scanning electron microscopy (SEM) as shown in Fig. 1. The Ti_2AlC, V_2AlC, Ta_2AlC, and Cr_2AlC MAX phases show stacked configurations with sheet-like layers, whereas other sets of MAX phases such as Ti_2SnC, Ti_3SiC_2 and Mo_2TiAlC_2 exhibited structures that were round and clumpy. The EDX spectral analysis confirmed the presence of the constituent elements (Fig. 1) and the elemental ratios calculated from atomic percentage followed the stoichiometry of the samples (Table S1).

The EDX elemental maps confirmed the uniform distribution of elements over the sample surface (Fig. S1).After analysis of the morphology and elemental compositions of the MAX phases, we further explored the properties of the materials as catalysts for the electrochemical splitting of water. Previous studies show that MAX/MAB

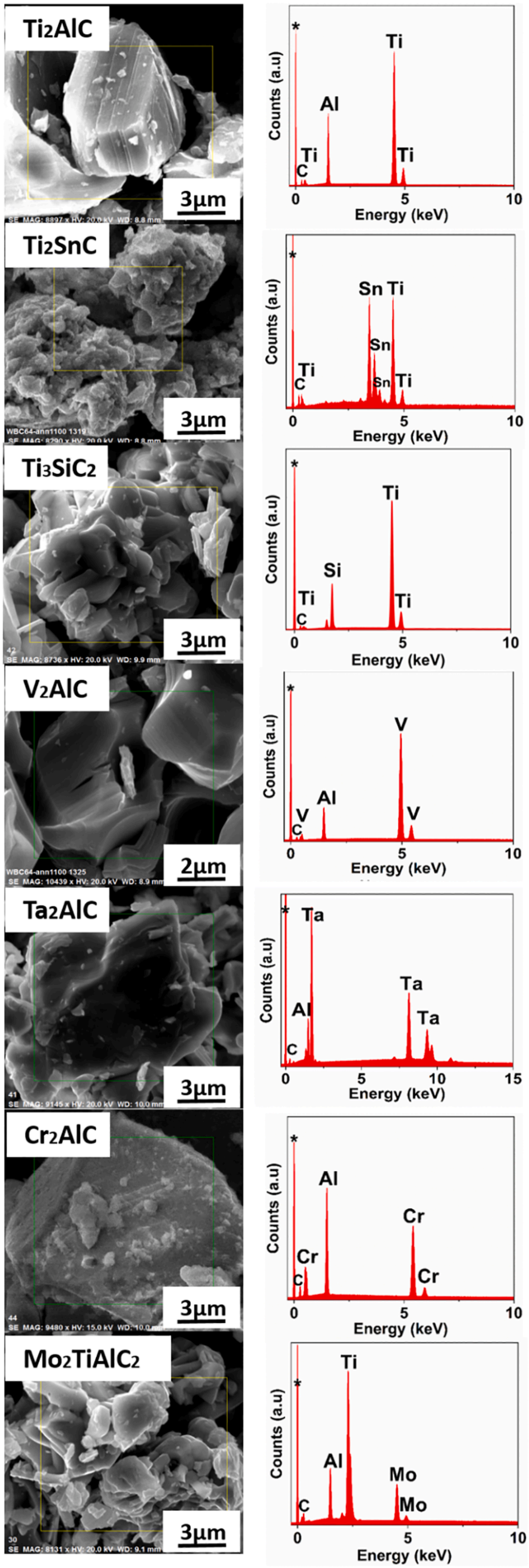

Fig. 1. SEM and EDX spectra of MAX phases.

phases possess catalytically active basal planes that make them ideal for electrochemical applications [25,37]. Linear sweep voltammetry (LSV) measurements were used to study the electrocatalytic performance of the MAX phase. Unmodified glassy carbon (GC) was used as a reference to evaluate the electrocatalytic performance of the materials. Overpotential at a current density of -1 mA cm^{-2} was used for comparison of the different phases, where a lower overpotential signifies better HER activity. LSV measurements of drop-casted MAX phases over GC electrode are shown in Fig. 2A, where the measured overpotentials of the MAX phases (Ti_2AlC, V_2AlC, Ta_2AlC, Cr_2AlC, Ti_2SnC, Mo_2TiAlC_2) were lower than GC, with the exception of Ti_3SiC_2 (-0.85 V vs. RHE).

The difference in the electrochemical behavior of the materials is related to the surface atoms. In Mo_2TiAlC_2, the Ti atoms are sandwiched between two molybdenum (Mo) layers that, in turn, are adjacent to the aluminum (Al) planes. This results in a Mo-Ti-Mo-Al-Mo-Ti-Mo stacking order with carbon atoms retaining their positions in the octahedral sites between the M layers [26]. The presence of Mo atoms over the outer layers of the M sites in Mo_2TiAlC_2 results in different surface properties compared to regular Ti-Alcontaining solid solutions [38] such as Ti_2AlC.. Thus, in Fig. 2A, we observe that Ti_2AlC has a higher overpotential (-0.76 V vs. RHE) and Mo_2TiAlC_2 a low overpotential (-0.57 V vs. RHE). In a study conducted by Anasori et al. on the ordered double-transition metal MXene, it was found that the electrochemical response of $Mo_2TiC_2T_x$ was dominated by the surface Mo layers [39]. The HER mechanism involved in these measurements was analyzed using the Tafel equation $\eta = b \log |j| + a$ (Fig. 2B), where η is the overpotential, j is the current density and b is the Tafel slope. Tafel slopes are determined by the rate-limiting steps of HER as follows [40-42]:

Adsorption (Volmer step):

$$H_3O^+ + e^- \rightarrow H_{ads} + H_2O;\ b \approx 120\ \text{mV dec}^{-1} \tag{1}$$

Desorption (Heyrovsky step):

$$H_{ads} + H_3O^+ + e^- \rightarrow H_2 + H_2O;\ b \approx 40\ \text{mV dec}^{-1} \tag{2}$$

Desorption (Tafel step):

$$H_{ads} + H_{ads} \rightarrow H_2;\ b \approx 30\ \text{mV dec}^{-1} \tag{3}$$

Ti_2SnC showed the lowest Tafel slope of 104 mV dec^{-1} while Ti_3SiC_2 had the highest Tafel slope value of 186 mV dec^{-1}. The Tafel slope values of the other MAX phases Mo_2TiAlC_2, V_2AlC, Cr_2AlC, Ta_2AlC, Ti_2AlC are 127, 127, 129, 129, and 138 mV dec^{-1} respectively. Thus, it could be inferred from the Tafel slope values that the rate-determining step of MAX phases is due to the Volmer adsorption process as the slope is around/more than 120 mV dec^{-1}.

The stability of the electrodes was evaluated using the chronoamperometry technique, where a constant potential needed to obtain -1 mA cm^{-2} of current density was applied based on LSV measurements in 0.5 M H_2SO_4. A rotating disk electrode (RDE) with a rotation speed of 600 rpm was used to measure the current continuously for 120 min to monitor the stability of the catalyst. The use of RDE involved continuous rotation of the working electrode to prevent blocking of the catalyst surface by the evolved gas bubbles. However, as the measurement proceeded the bubbles continued to hinder the active area, leading to a rapid decay in the current [43]. The fluctuations in current are observed when the bubbles are removed/formed during the reaction (Fig. S2A–C). For the analyzed MAX phases, the catalyst was found to be stable only for a very short time. In general, the above observations suggest that the MAX phases possess intermediate electrocatalytic performance compared to other reported layered materials.

4. Conclusions

In summary, various combinations of elements from the periodic table result in changes to the electronic structure of the material and in turn alter its catalytic and electrochemical properties. Morphological analysis of these layered materials using SEM provided an overview of the material. The electrocatalytic activity of MAX phases (Ti_2AlC, V_2AlC, Ta_2AlC, Cr_2AlC, Ti_2SnC, Mo_2TiAlC_2, and Ti_3SiC_2) was successfully analysed using linear sweep voltammetry (LSV). Molybdenum containing layered ternary carbide (Mo_2TiAlC_2) showed a low overpotential at a current density of -1 mA cm^{-2} while Ti_3SiC_2 showed a high overpotential. New materials will play a vital role in the development of novel, low-cost and efficient electrocatalysts for HER to fuel a sustainable energy system in the future.

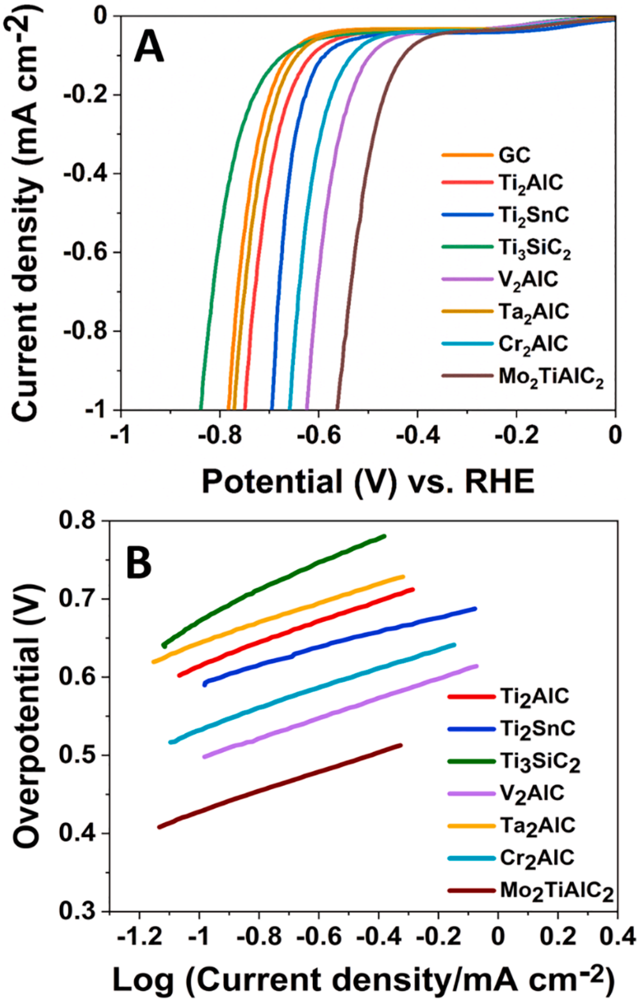

Fig. 2. (A) Linear sweep voltammograms of GC, MAX phases at a scan rate of 5 mV s^{-1}. (B) Tafel plots of MAX phases.

CRediT authorship contribution statement

K.P. Akshay Kumar: Investigation, Methodology, Formal analysis, Data curation, Validation, Writing - original draft. **Osamah Alduhaish:** Conceptualization, Analysis, Discussion. **Martin Pumera:** Conceptualization, Resources, Supervision.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.elecom.2021.106977.

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