



**Interfacial Charge Transfer Driven by Surface Termination-
Controlled Ti₂C MXene for Enhanced Hydrogen Storage in
Magnesium**

Journal:	<i>Journal of Materials Chemistry A</i>
Manuscript ID	TA-COM-07-2024-004563.R1
Article Type:	Communication
Date Submitted by the Author:	12-Aug-2024
Complete List of Authors:	Kim, Min Gyu; Korea Advanced Institute of Science and Technology, Department of Chemical and Biomolecular Engineering Kang, ShinYoung; Lawrence Livermore National Laboratory Wood, Brandon; Lawrence Livermore National Laboratory Cho, Eun Seon; Korea Advanced Institute of Science and Technology, Department of Chemical and Biomolecular Engineering

ARTICLE

Interfacial Charge Transfer Driven by Surface Termination-Controlled Ti₂C MXene for Enhanced Hydrogen Storage in Magnesium

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Min Gyu Kim^a, ShinYoung Kang^b, Brandon C. Wood^b, and Eun Seon Cho^{*a}

Two-dimensional transition metal carbides and nitrides (MXenes) with layered structure and high conductivity have been effectively utilized in various energy materials, including as a catalytic support of MgH₂ for hydrogen storage. However, the terminal groups formed on the surface during etching step tend to deactivate reactive Mg metal and add dead mass, thereby deteriorating the catalytic role of MXene in hydrogen sorption of Mg. We exploited a molten-salt derived MXene with easily modifiable –Cl terminations, compared to conventional –O, –OH and –F groups, and synthesized a composite of Mg and delaminated Ti₂CCl_x MXene to improve hydrogen storage performance of Mg through charge transfer. This strategy enables the formation of intimate interface between Mg and MXene, facilitating charge transfer and thereby boosting catalytic effect. The resulting composite demonstrates significantly enhanced hydrogen sorption kinetics by modulating Mg–H bond strength. This novel approach of modifying surface terminations leverages the unique properties of MXene as a superior support for active materials, offering broader applications in energy materials.

1. Introduction

With growing apprehensions on the environmental impact of CO₂ emission, substituting traditional fossil fuels to renewable energy sources is imperative.^{1, 2} Hydrogen stands out as a promising energy carrier due to its high energy density, clean-burning feature and versatility, thereby enabling us to store a tremendous amount of energy generated from renewable sources. The efficient storage of hydrogen is a crucial aspect that impacts its viability as a widespread energy carrier.³ Solid-state hydrogen storage offers considerable benefits compared to conventional pressurized gas or liquefied hydrogen storage in terms of safety and efficiency.⁴ Particularly, magnesium hydride (MgH₂) has advantages of its high theoretical gravimetric capacity (7.6 wt. %), good reversibility and abundant natural resources,⁵⁻⁷ while it faces major challenges such as high operating temperature requirements and sluggish reaction kinetics due to a strong Mg–H bonding nature.^{8, 9}

Introducing catalytic additives to MgH₂ such as transition metals¹⁰⁻¹², their corresponding oxides^{13, 14} and carbides^{15, 16} is one of the feasible strategies to improve its hydrogen storage properties by providing additional activation sites or reaction pathway for hydrogen.¹⁷ Recently, Two-dimensional (2D)

transition metal carbides and nitrides (MXenes) have been found to show a great catalytic activity for enhancing hydrogen sorption property of MgH₂.¹⁸⁻²¹ Compared to typical transition metal-based catalysts which are sporadically doped within MgH₂ as clusters,¹⁸ atomically thin 2D structured MXene offers the potential to effectively provide a number of active catalytic sites at the interface with MgH₂. Although previous studies have shown the validity of MXene as a catalyst for MgH₂, the underlying mechanism behind the catalytic effect is not adequately understood.²² Particularly, the studies on Ti-based MXene have suggested that the metallic Ti acts as a key catalytic component by forming an intermediate titanium hydride phase.^{18, 21, 23} However, as metallic Ti is precipitated out of carbide structure, the 2D structure and properties as a metal-carbon composite might undergo changes, causing it to lose its identity and ceasing its role as a distinct nanomaterial. Apart from the effect of precipitated Ti, the catalytic role of MXene as a metal-carbide have been investigated through computational simulations, yet corresponding experimental observations are currently lacking.²⁴⁻²⁶

On the other hand, during MAX phase etching reaction for synthesis of MXene, terminal groups such as =O, –OH, –F are inevitably formed on the surface.^{27, 28} However, upon compositing with Mg for the aforementioned catalytic effect, Mg is susceptible to oxidation with these groups, resulting in a possible creation of passivation layers which hinder the reaction kinetics and reduce active mass.²¹ To avoid such issues, a post-modification on surface termination of MXene is essential, while the robust Ti–O and Ti–F bonds introduced during the etching step in acid media make it challenging to replace surface groups through a post-synthetic route.²⁹ A newly developed synthetic method produces MXenes with –Cl and –Br

^a Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea. E-mail: escho@kaist.ac.kr

^b Laboratory for Energy Application for the Future (LEAF), Lawrence Livermore National Laboratory, Livermore, California 94550, United States. E-mail: kang10@llnl.gov

† Electronic Supplementary Information (ESI) available: All experimental and theoretical details, and additional characterization experiments. See DOI: 10.1039/x0xx00000x

terminations by using a molten salt, in place of oxygen or fluorine.²⁹⁻³¹ The Ti–Cl and Ti–Br bonds are relatively labile and can be substituted or eliminated to create a variety of MXene derivatives.^{29, 32} Despite such development, the studies about elimination of surface termination from MXene remains limited in using LiH as a reducing agent assisted by molten-salt, which involves multiple steps and harsh reaction conditions.²⁹

In this work, we present a facile synthesis of MXene with the removal of –Cl terminal group (denoted as –Cl_x) via a molten-salt etching method for boosting the catalytic effect on hydrogen sorption kinetics of Mg upon the formation of composite (Mg@DL-Ti₂CCl_x) with delaminated Ti₂CCl₂ MXene (DL-Ti₂CCl₂). The synthesized composite allows the formation of Ti–Mg interface which has a catalytic effect on the hydrogen storage property of MgH₂. Interestingly, charge redistribution occurs between MgH₂ and DL-Ti₂CCl_x, resulting in a weakening of the strength of the Mg–H bond strength, which in turn improves hydrogen sorption properties. Additionally, DFT calculations also show that the strength of the interaction depended on the amount of –Cl present, with a lower –Cl

content resulting in a stronger interaction. This implies that controlling the terminal groups of MXene is crucial for further enhancing its catalytic function as a support for MgH₂.

2. Results and discussion

The synthesis of Mg@DL-Ti₂CCl_x involves several key steps, as illustrated in Figure 1a. Multilayer-Ti₂CCl₂ (ML-Ti₂CCl₂) was prepared from MAX phase via a modified molten-salt etching method.^{29, 30} This was followed by delamination with lithium pyrene (LiPy) to form DL-Ti₂CCl₂, and simultaneous reduction of DL-Ti₂CCl₂ and Mg²⁺ precursor was performed to form Mg@DL-Ti₂CCl_x (see Supporting Information for the detailed procedure). The scanning electron microscopy (SEM) image of ML-Ti₂CCl₂ in Figure 1b shows a distinctive lamellar microstructure formed by the removal of Al layer from Ti₂AlC MAX phase and the decoration with –Cl terminal groups from the chloride salt. The SEM image (Figure S1a) of Ti₂AlC MAX phase displays a combined structure of Ti₂AlC and excess metal (Ti, Al) precursors,^{30, 33} which are eliminated during the etching step.

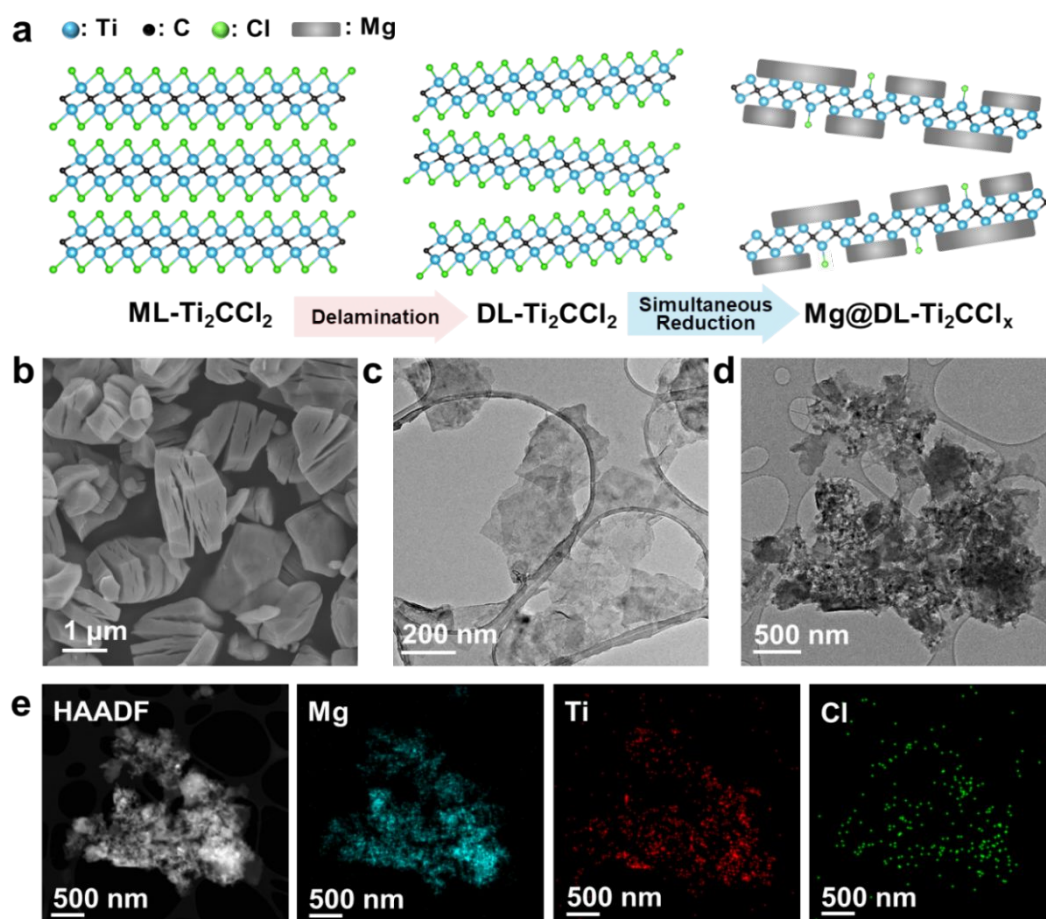


Figure. 1 Scheme and morphology change of MXene and Mg composite by each synthetic step. (a) Schematic illustration of Mg@DL-Ti₂CCl_x composite preparation. (b) Scanning electron microscopy (SEM) image of ML-Ti₂CCl₂. Transmission electron microscopy (TEM) image of (c) DL-Ti₂CCl₂ and (d) Mg@DL-Ti₂CCl_x. (e) High-angle annular dark-field (HAADF) image of Mg@DL-Ti₂CCl_x and energy-dispersive X-ray spectroscopy (EDS) mapping of Mg, Ti and Cl representing evenly distributed Mg over the DL-Ti₂CCl_x.

Despite the absence of the Al layer, the ML-Ti₂CCl₂ MXene synthesized via the molten-salt etching method maintains a laminated structure due to van der Waals forces, posing challenges for good dispersion during solution-based synthesis and full utilization of its large surface area. Thus, a delamination process is employed, exposing the -Cl terminated basal plane on the surface before the composite synthesis. In the previous studies, molten-salt etched MXenes were delaminated using *n*-butyllithium (*n*-BuLi),^{29, 34} which has been widely used for transition-metal dichalcogenides via Li⁺ ion intercalation.^{35, 36} However, a pyrophoric feature of *n*-BuLi could pose a substantial safety hazard, especially when produced in a large scale for hydrogen storage system. In this work, we employed lithium pyrene (LiPy) for safe and more effective delamination procedure, in which Li⁺ ions are intercalated into ML-Ti₂CCl₂ layers owing to a lower redox potential, enabling a successful delamination via a simple ultrasonication.³⁷ The two-dimensional structure of the delaminated-Ti₂CCl₂ (DL-Ti₂CCl₂) is shown by transmission electron microscopy (TEM) and SEM images (Figure 1c, S1b). The DL-Ti₂CCl₂ forms a stable colloidal solution in a polar solvent like *N*-methyl formamide (Figure S1c), and its hexagonal crystallinity is retained after delamination process as shown in the selected area electron diffraction (SAED) pattern (Figure S2).

To synthesize Mg@DL-Ti₂CCl_x composite, a strong reducing agent—lithium biphenyl (LiBp)—was utilized in this work. In addition to reducing Mg²⁺ precursor to Mg nanoparticles,^{38, 39} LiBp also partially eliminates the -Cl terminations from the DL-Ti₂CCl₂ surface, forming DL-Ti₂CCl_x, which will be discussed in the later section. This removal of -Cl functional groups exposes the titanium carbide surface, facilitating the formation of a direct Ti-Mg catalytic interface. In other words, the synthesis of Mg@DL-Ti₂CCl_x is accomplished through the removal of -Cl terminal group from DL-Ti₂CCl₂ layer along with a simultaneous reduction of Mg²⁺ precursors using LiBp. The high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) with energy-dispersive X-ray spectroscopy (EDS) and bright-field TEM images (Figure 1d, e) show the composite of Mg and DL-Ti₂CCl_x, demonstrating that Mg is homogeneously decorated on DL-Ti₂CCl_x over the Mg@DL-Ti₂CCl_x composite with residual -Cl termination (Figure 1e).

To elucidate the effect of LiBp treatment on the elimination of -Cl termination, the MXenes—ML-Ti₂CCl₂ and DL-Ti₂CCl₂—were solely treated with LiBp. The SEM EDS spectra shows that the amount of elemental Cl over Ti₂CCl₂ layers is significantly reduced with the LiBp treatment to form ML-Ti₂CCl_x (Figure S3 and Table S1). In the subsequently obtained X-ray diffraction (XRD) pattern (Figure S4a), the (1120) peak whose position highly depends on the surface termination is shifted from 57.0° to 60.2°, implying the change of terminal groups.²⁹ In addition, the substantially reduced (0001) peak and the shifted (1120) peak to 60.2° are consistent with the previously reported result on bare-Ti₂C, in which case the terminal groups were found to be completely removed.²⁹ The reduction of the peak assigned to -Cl termination in the Raman spectra also supports that the LiBp treatment is effective for removal of -Cl termination (Figure S4b). The *c* lattice parameters were acquired from the

high-resolution TEM (HRTEM) image for both ML-Ti₂CCl₂ and ML-Ti₂CCl_x, which are *c* = 8.76 Å and *c* = 10.46 Å, respectively (Figure S4c, d), closely aligned with the reported values in the literature.²⁹ The *c* lattice parameter of ML-Ti₂CCl₂ is consistent with XRD result, as shown in Figure S4a, while the *c* value increases upon the LiBp-treatment because of space group change from *P-3m1* to *P63/mmc*. The change in Ti-C bond with the loss of the -Cl terminal group was investigated by the X-ray photoelectron spectroscopy (XPS) analysis in DL-Ti₂CCl₂ which was used during synthesis in delaminated form (Figure S5). The peaks for the Ti-C bond are shifted to the lower binding energies in both the Ti 2*p* and C 1*s* regions as the electronegative element Cl disappears. Additionally, the Ti with higher oxidation state is observed, attributed to the amorphous Ti oxide on the surface, which is reduced by LiBp-treatment. It is noteworthy that the conventional approaches to modifying functional groups over MXene require high temperatures (300–600 °C)^{21, 40} or molten-salt assisted reactions,²⁹ whereas LiBp readily removes functional groups under a mild condition. Even though a non-negligible amount of Cl is detected on the SEM-EDS analysis of ML-Ti₂CCl_x (Figure S3 and Table S1) and TEM-EDS mapping of DL-Ti₂CCl_x (Figure S6), the -Cl removal is quite evident and is thought to be sufficient to expose a bare Ti surface.

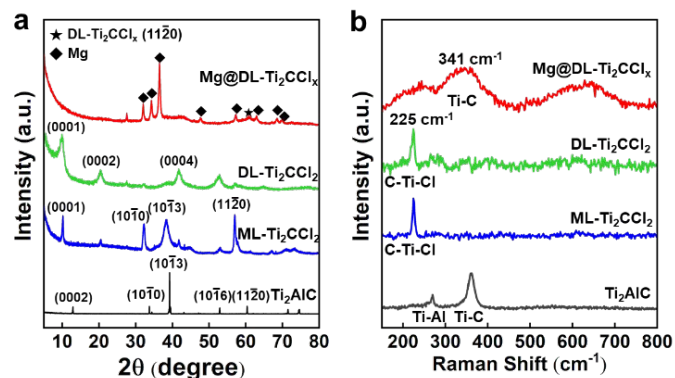


Figure 2 Change of crystalline and chemical structure of Ti₂AlC MAX phase, ML-Ti₂CCl₂, DL-Ti₂CCl₂ and Mg@DL-Ti₂CCl_x composite based on (a) X-ray diffraction (XRD) patterns and (b) Raman spectra.

The change of crystalline structure and terminal group over MXene were further investigated. The powder XRD pattern of ML-Ti₂CCl₂ shows distinct peaks corresponding to Ti₂CCl₂, indicating the complete etching of the Al layer from the Ti₂AlC MAX phase.^{29, 34} Prior to the delamination to form DL-Ti₂CCl₂, an expansion in interlayer spacing is observed in ML-Ti₂CCl₂ due to Li⁺ intercalation, shifting the (0001) peak from *c* = 8.67 Å to *c* = 8.88 Å (Figure S7).²⁹ The DL-Ti₂CCl₂ shows a series of (000*l*) basal plane peaks since the delaminated sheets are horizontally aligned by vacuum-filtration.^{29, 41} The Mg@DL-Ti₂CCl_x shows a clear characteristic metallic Mg pattern with the (1120) peak of LiBp-treated Ti₂CCl₂, indicating the simultaneous partial removal of -Cl terminal group. The formation of the composite was also confirmed by SAED, which shows a clear single-crystalline pattern from DL-Ti₂CCl_x and polycrystalline ring from decorated Mg particles (Figure S8). The change of surface

termination on MXene was also identified through Raman spectroscopy (Figure 2b). The out-of-plane vibration of Ti–C with –Cl termination is observed at 225 cm^{-1} (A_{1g}) for ML-Ti₂CCl₂.³⁴ The DL-Ti₂CCl₂ retains the A_{1g} peak at 225 cm^{-1} which indicates that –Cl termination is well preserved during delamination process, while Mg@DL-Ti₂CCl_x shows the peak at 341 cm^{-1} (A_{1g}) which corresponds to the out-of-plane stretching mode of Ti–C without surface termination,⁴² and the A_{1g} peak associated with the –Cl termination at 225 cm^{-1} is significantly diminished. These results suggest that most of –Cl terminal groups are removed under the highly reductive environment with LiBp, thereby allowing the direct interaction of Mg with Ti atoms in MXene.

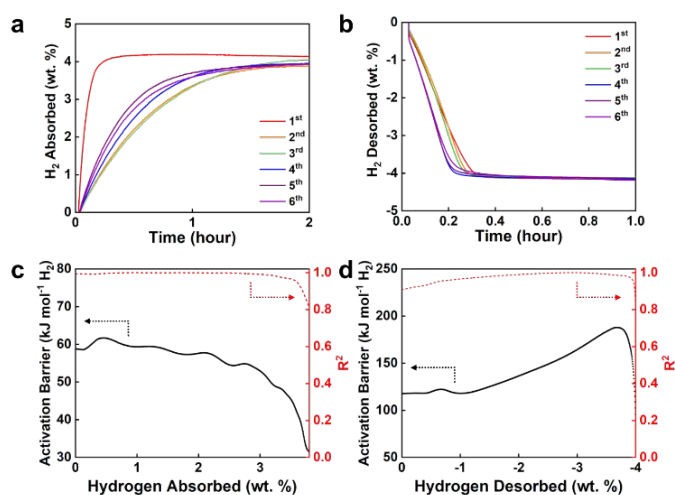


Figure 3 Hydrogen sorption kinetics of Mg@DL-Ti₂CCl_x composite. (a) Isothermal hydrogen absorption at 200 °C under 15 bar of H₂ and (b) hydrogen desorption at 300 °C under 0 bar of H₂. Activation barrier for (c) absorption and (d) desorption as a function of absorbed and desorbed wt. % H₂, respectively.

In order to examine the hydrogen sorption properties of Mg@DL-Ti₂CCl_x, isothermal ab/desorption kinetics was measured with Sievert's apparatus (Figure 3a-b). In the first cycle, 4.1 wt. % of H₂ is absorbed within 20 min; however, the kinetics gets sluggish in the subsequent cycle, while its rate is maintained afterwards. On the other hand, the desorption is completed within 20 minutes and maintained a stable rate. To understand these phenomena, we consider the hydrogen sorption process of Mg metal. The H₂ absorption follows several sequential steps: (1) dissociation of hydrogen molecule on the surface, (2) diffusion of hydrogen atom into metal and (3) nucleation and growth of hydride phase. Reversely, desorption from MgH₂ involves: (1) formation of metallic Mg phase, (2) diffusion of hydrogen atom from hydride phase to metallic Mg phase and (3) recombination of hydrogen atoms to form hydrogen molecule.^{43, 44} It can be assumed that the absorption rate decreases since Mg particles are sintered during the H₂ ab/desorption cycle.^{45, 46} Since MgH₂ melts at a lower temperature (327 °C) compared to Mg (650 °C), sintering is likely occur in the hydrogenated state. Increased Mg grain size reduces surface area for hydrogen dissociation and slows hydrogen atom diffusion to the grain core.^{47, 48} The grain size growth is also evident in the XRD result (Figure S9a), in which

the initially broad Mg peaks for as-synthesized Mg@DL-Ti₂CCl_x becomes narrow after H₂ sorption cycles, yet the characteristic (1120) MXene peak is preserved which shows that DL-Ti₂CCl_x retains its structure (Figure S9b). The sintering primarily occurs during the initial cycle, possibly because the DL-Ti₂CCl_x within the composite acts as a physical barrier, preventing further excessive sintering once it reaches a certain equilibrium state. The structural stability is confirmed by preservation of the hexagonal crystallinity of DL-Ti₂CCl_x in the composite after hydrogen sorption cycle, shown in the SAED pattern (Figure S10).

Nevertheless, the desorption rate of Mg@DL-Ti₂CCl_x is not significantly affected as the hydrogen cycle proceeds, compared to the absorption (Figure 3b). It is assumed that this unusual discrepancy arises from the different reaction mechanism governing hydrogen ab/desorption process. Typically, MgH₂ undergoes a localized charge transfer step between Mg²⁺ and H⁻ during desorption.^{49, 50} However, due to the lack of free electrons in the conduction band of semi-conductive MgH₂ at the fully hydrogenated state, the nucleation of metallic Mg should be preceded which is commonly referred as an incubation period.⁵⁰⁻⁵² Interestingly, the desorption of Mg@DL-Ti₂CCl_x shows negligible incubation time at the initial desorption stage. We speculate that the high electrical conductivity of DL-Ti₂CCl_x, especially at the –Cl removed region,⁵³ allows it to act as a charge transfer intermediate, facilitating hydrogen recombination without prior incubation period. For a comparison, we additionally synthesized the composite of Mg and conventional Ti₂CT_x (T = –O, –OH and –F) MXene instead of DL-Ti₂CCl₂ (Mg@Ti₂CT_x). In the isothermal hydrogen ab/desorption of Mg@Ti₂CT_x, it is observed that the rate gradually decreases for both cases, along with a typical incubation period at the initial stage of desorption, as opposed to Mg@DL-Ti₂CCl_x (Figure S11). This suggests that the catalytic activity of Ti₂CT_x is deteriorated as the hydrogen cycle progresses, which implies the collapse of the Ti₂CT_x MXene structure. MXene synthesized with an acid solution contains F-ions (LiF/HCl or HF), and it might become structurally unstable because of the formation of atomic defects.^{27, 54} Hence, unlike DL-Ti₂CCl_x, Ti₂CT_x might be more vulnerable under hydrogen cycle environment, potentially leading to the loss of its catalytic function and its role as a physical barrier. Furthermore, it was reported that MXene with a terminal group could cause the formation of a passivation layer at the interface of Mg,²¹ suggesting that the elimination of terminal groups is crucial when creating the composite of Mg and MXene. Despite using LiBp as a reducing agent, a removal of terminal groups from conventional Ti₂CT_x is difficult to be achieved, supported by SEM-EDS analysis and Raman spectroscopy (Figure S12 and Table S2). Unlike ML-Ti₂CCl₂, the terminal groups mostly remain, and the both out-of-plane vibration (A_{1g}) and in-plane vibration of Ti–C (E_g) with terminal groups are observed. Presumably, a harsher condition is required to break the terminal groups attached to Ti₂CT_x. The key factor for creating an efficient catalytic interface lies in the utilization of –Cl decorated MXene and its subsequent removal through LiBp treatment, as demonstrated in this study.

In order to further probe the hydrogen sorption kinetics of $\text{Mg@DL-Ti}_2\text{CCl}_x$, we evaluated activation energies by fitting hydrogen ab/desorption kinetic curves at three different temperatures (Figure S13) to the Arrhenius law (Figure 3c, d) and Johnson–Mehl–Avrami (JMA) equation (Figure S14, S15). The hydrogen ab/desorption kinetic curves and activation barrier plots solely based on the mass of Mg are additionally shown in Figure S16, while the overall trend tends to be consistent with the one based on the total composite mass. During absorption, $\text{Mg@DL-Ti}_2\text{CCl}_x$ displays the lower activation energy values than the barriers identified in previous studies on hydrogen dissociation on Mg surface ($E_a \approx 83.9\text{--}101.3 \text{ kJ mol}^{-1} \text{ H}_2$)^{55–57} and H atom diffusion through MgH_2 ($E_a \approx 95.5 \text{ kJ mol}^{-1} \text{ H}_2$).^{58, 59} Thus, we anticipate that the energy barrier on both surface and bulk processes are alleviated on the hydrogen absorption kinetics of the $\text{Mg@DL-Ti}_2\text{CCl}_x$. The activation energy acquired from JMA equation ($E_a \approx 53.5 \text{ kJ mol}^{-1} \text{ H}_2$) is also aligned with it, while providing additional information regarding the dimensionality of the growth. The best fitting was obtained with Avrami exponent (n) of $n = 1.0$, indicating that the growth of MgH_2 occurs in one-dimensional geometry which can be described by hydrogen diffusion through lattice vacancies followed by thickening of MgH_2 layer in one-dimension as proposed in literatures.^{60, 61} Furthermore, the activation energy desorption for $\text{Mg@DL-Ti}_2\text{CCl}_x$ determined from both Arrhenius law (Figure 3d) and JMA equation (Figure S15d) is found to be lower than that for other Mg composites ($E_a \approx 140\text{--}219 \text{ kJ mol}^{-1} \text{ H}_2$)^{59, 62–64} which are synthesized through the similar Rieke method.⁶⁵ This improvement on desorption kinetics is believed to be originated from the weakening of the Mg–H bond caused by charge transfer which will be discussed later. A notable

characteristic is that the n value of desorption kinetics from the JMA fitting displays a non-integer value ($n = 0.5\text{--}0.7$). This suggests that the desorption process may occur via diffusion-controlled one-dimensional growth with instantaneous nucleation which aligns with negligible incubation period as described previously.⁶⁶

To unravel the in-depth catalytic effect of $\text{DL-Ti}_2\text{CCl}_x$ on the hydrogen storage performance of $\text{Mg@DL-Ti}_2\text{CCl}_x$ at the interface of Ti–Mg, the change of chemical state before and after H_2 sorption cycles was investigated through XPS analysis (Figure 4a, b). As-synthesized $\text{Mg@DL-Ti}_2\text{CCl}_x$ exhibits a comparable binding energy for Ti–C bond to $\text{DL-Ti}_2\text{CCl}_x$ in both Ti 2*p* and C 1*s* spectra (Figure S5a, b); however, the relevant peaks are shifted to the lower binding energy after hydrogen sorption cycling, which clearly shows the charge redistribution in $\text{Mg@DL-Ti}_2\text{CCl}_x$ composite which was induced during the cycling with the existence of Mg. The consistent shift of the Ti–C peak to a lower binding energy in the Ti 2*p* and C 1*s* XPS results indicates that charge transfer from Mg to Ti–C has occurred. The retention of the transition metal related peak in the C 1*s* spectra after hydrogen sorption process indicates that the Ti–C bonding is well-preserved. This aligns with the earlier explanation of structural stability. In addition, the hexagonal crystallinity of $\text{DL-Ti}_2\text{CCl}_x$ in the composite is well maintained after hydrogen sorption cycle (Figure S10). This structural stability is attributed to the molten-salt etching method, wherein hydrofluoric acid (HF) was intentionally excluded from the synthesis process. To the best of our knowledge, our study is the first experimental demonstration of this distinct charge transfer between Mg and Ti–C in composite of Mg and MXene. This charge transfer effect was further supported by Ti *L*-edge near edge X-ray absorption fine structure (NEXAFS) and Raman spectroscopy (Figure 4c, d).^{67, 68} The Ti *L*-edge spectrum is related to electron excitation from Ti 2*p*_{3/2} (*L*₃) and 2*p*_{1/2} (*L*₂) core levels to 3*d* states. As the 3*d* orbital energy level is split by the crystal field effect, each Ti *L*₃ edge and *L*₂ edge is further divided into *t*_{2*g*} and *e*_g subpeaks.⁶⁹ In the hydrogen cycled sample, the *t*_{2*g*} peaks become more intense at the both *L*₂ and *L*₃ edge, accompanied with the loss of the clear splitting and a shift of the pre-edge towards the lower energy, indicating a lower oxidation state of Ti in MXene.^{70–72} The observation of a blue shift (341 cm^{-1} to 360 cm^{-1}) in the *A*_{1*g*} peak, associated with the Ti–C stretching mode in the the Raman spectra of hydrogen cycled sample (Figure 4d), suggests a strengthening of the Ti–C bond due to the charge transfer.⁶⁷ These results confirm the charge transfer between $\text{DL-Ti}_2\text{CCl}_x$ and Mg, which suggests that $\text{DL-Ti}_2\text{CCl}_x$ may perturb the Mg–H bonds for the dehydrogenation of MgH_2 .

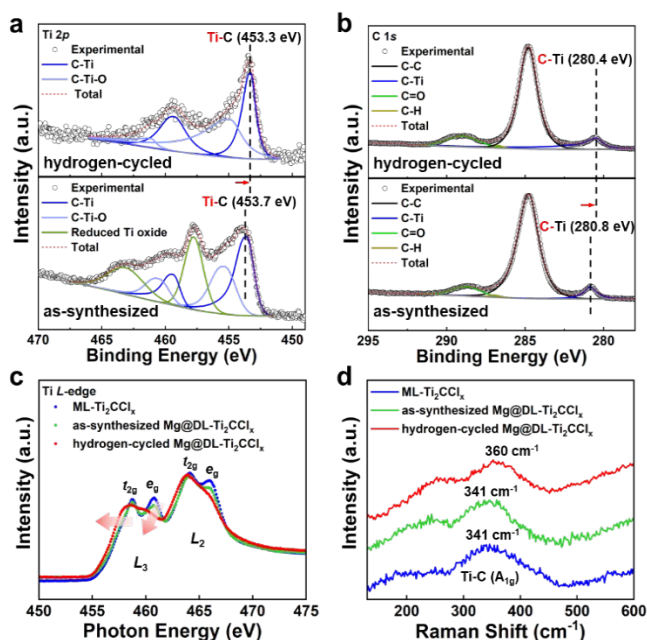


Figure 4 Charge transfer between $\text{DL-Ti}_2\text{CCl}_x$ and Mg. (a) Ti 2*p* and (b) C 1*s* XPS spectra of as-synthesized $\text{Mg@DL-Ti}_2\text{CCl}_x$ (below) and hydrogen-cycled $\text{Mg@DL-Ti}_2\text{CCl}_x$ (upper). (c) Ti *L*-edge NEXAFS and (d) Raman spectra of $\text{ML-Ti}_2\text{CCl}_x$, as-synthesized and hydrogen-cycled $\text{Mg@DL-Ti}_2\text{CCl}_x$.

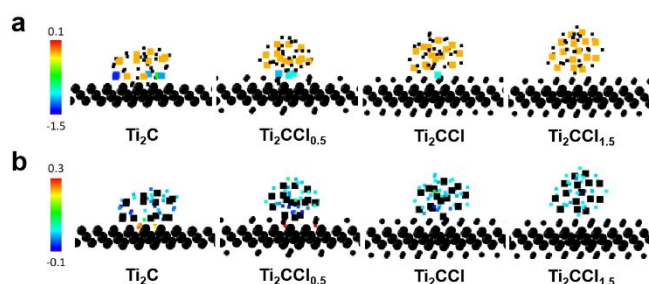


Figure 5 Changes in the Bader charge of (a) Mg atoms and (b) H atoms in the $\text{MgH}_2@DL\text{-Ti}_2\text{CCl}_x$ interface models evaluated based on the DFT calculations. Mg and H atoms are denoted by large and small squares, respectively. Circles are Ti, C, and Cl atoms in MXene sheets. Atoms of interest (Mg in (a) and H in (b)) are colored by their valence state change: reddish color indicates electron loss (oxidation), and bluish color indicates electron gain (reduction). Other atoms are colored in black for simplicity.

To further elucidate the impact of $DL\text{-Ti}_2\text{CCl}_x$ on the MgH_2 desorption kinetics, we conducted the density functional theory (DFT) calculations,^{73, 74} in which structures and charge densities were analyzed using the interface models between MgH_2 nanoparticle and $DL\text{-Ti}_2\text{CCl}_x$ sheet ($x = 0.0, 0.5, 1.0, \text{ and } 1.5$) that are visualized in Figure S17. The Bader charge analysis calculates the number of electrons belonging to each atom by defining atomic volume within which the charge density is integrated.⁷⁵⁻⁷⁸ We also computed the Bader charge state of isolated MgH_2 nanoparticles free from MXene as a reference. Figure 5 displays the Bader charge difference in Mg and H atoms before and after forming the interface, *i.e.*, changes in the number of electrons when forming the $\text{MgH}_2@Ti_2CCl_x$ interface compared to the isolated MgH_2 nanoparticles. For Mg, centering from the orange color where the atomic charge is invariant, positive change (reddish color) and negative change (bluish color) indicate oxidation and reduction, respectively. The impact of Ti_2CCl_x is most prominent when the $-Cl$ terminal group is completely removed. Many interface Mg atoms obtain additional electrons, which is from Mg^{2+} in MgH_2 towards the fully desorbed Mg^0 metal. Similarly, H^- ions in MgH_2 oxidize towards H^0 near Ti_2C , which can easily recombine into H_2 molecule. The charge redistribution phenomenon due to Ti_2CCl_x slowly diminishes in the presence of the $-Cl$ terminations, and eventually the Mg and H atoms do not feel the $\text{MgH}_2@Ti_2CCl_x$ interface at $x = 1.5$. Besides the charge redistribution within the MgH_2 particle, Ti_2CCl_x also participates in the charge transfer (Figure S18). However, given that atoms in Ti_2CCl_x undergo both oxidation and reduction due to the complexity in the local environment, it is not clear that the role of Ti_2CCl_x is monolithic in charge transfer. More systematic investigation exploring various contact area, distance, and local environment at the $\text{MgH}_2@Ti_2CCl_x$ interface is demanded for clarification, which is beyond the scope of this work. Nonetheless, the impact of charge redistribution within MgH_2 is clear to the deformation of its structure. Reduction of Mg and oxidation of H elongates the Mg–H bond from 1.88 Å to 1.91 Å in the $\text{MgH}_2@Ti_2C$ (Figure S19), suggesting that Ti_2CCl_x facilitates the initial step of desorption,

namely Mg–H bond breakage, and it eventually leads to improved desorption rates as observed in experiments. Our simulation also supports the efficacy of LiBp treatment which helps eliminating the $-Cl$ terminations to maximize the catalytic activity of Ti_2CCl_x .

3. Conclusions

In summary, this study demonstrates the role of $DL\text{-Ti}_2\text{CCl}_x$ MXene in enhancing the hydrogen storage property of Mg via the formation of an intimate interface with Ti-exposed $DL\text{-Ti}_2\text{CCl}_x$. Such interface allows an efficient charge transfer between Mg and Ti, attributed to the removal of surface termination groups over MXene, and it is enabled by introducing relatively weak $-Cl$ terminations to the Ti atoms using molten-salt etching method, in contrast to the previously reported approaches which require harsh conditions. The identical reduction process was employed for incorporating Mg particles, leading to the one-pot synthesis of the $\text{Mg}@DL\text{-Ti}_2\text{CCl}_x$ composite. The composite exhibits improved hydrogen desorption property of MgH_2 , primarily due to the charge transfer from Mg to $DL\text{-Ti}_2\text{CCl}_x$, which reduces the strength of the Mg–H bond at the interface. Furthermore, due to the excellent electrical conductivity of Ti_2CCl_x , it potentially serves as an electron mediator, facilitating electron transfer at the initial stage of desorption and thus reducing the incubation period. This work provides a novel approach for synthesizing Mg–MXene complexes for efficient hydrogen storage medium and elucidates the charge transfer at the Ti–Mg interface. This strategy can be applied to other energy materials, such as those used in energy storage, catalysis, to improve its performance through the formation of well-defined interface and electronic structure control.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National R&D Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (NRF-2022K1A4A8A01080242 and NRF-2022M3D1A2095314). A part of this work was supported by the Hydrogen Materials Advanced Research Consortium (HyMARC), established as part of the Energy Materials Network by the U.S. Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy (EERE), Hydrogen and Fuel Cell Technologies Office, and was performed under the auspices of the DOE by Lawrence Livermore National Laboratory (LLNL) under Contract No. DE-AC52-07NA27344. Part of the research was performed using computational resources sponsored by the DOE's EERE and located at the National Renewable Energy Laboratory. We also acknowledge computational resources at Livermore Computing at LLNL.

Notes and references

- N. L. Panwar, S. C. Kaushik and S. Kothari, *Renewable Sustainable Energy Rev.*, 2011, **15**, 1513-1524.
- J. Rockström, O. Gaffney, J. Rogelj, M. Meinshausen, N. Nakicenovic and H. J. Schellnhuber, *Science*, 2017, **355**, 1269-1271.
- S. Niaz, T. Manzoor and A. H. Pandith, *Renewable Sustainable Energy Rev.*, 2015, **50**, 457-469.
- S. McQueen, J. Stanford, S. Satyapal, E. Miller, N. Stetson, D. Papageorgopoulos, N. Rustagi, V. Arjona, J. Adams and K. Randolph, *Department of energy hydrogen program plan*, US Department of Energy (USDOE), Washington DC (United States), 2020.
- Y. Wang and Y. Wang, *Prog. Nat. Sci.: Mater. Int.*, 2017, **27**, 41-49.
- T. Sadhasivam, H.-T. Kim, S. Jung, S.-H. Roh, J.-H. Park and H.-Y. Jung, *Renewable Sustainable Energy Rev.*, 2017, **72**, 523-534.
- D. J. Han, K. R. Bang, H. Cho and E. S. Cho, *Korean Journal of Chemical Engineering*, 2020, **37**, 1306-1316.
- Y. Sun, C. Shen, Q. Lai, W. Liu, D.-W. Wang and K.-F. Aguey-Zinsou, *Energy Stor. Mater.*, 2018, **10**, 168-198.
- H. Wang, H. Lin, W. Cai, L. Ouyang and M. Zhu, *J. Alloys Compd.*, 2016, **658**, 280-300.
- G.-x. Liang, J. Huot, S. Boily, A. Van Neste and R. Schulz, *J. Alloys Compd.*, 1999, **292**, 247-252.
- C. Zhou, J. Zhang, R. C. Bowman Jr and Z. Z. Fang, *Inorganics*, 2021, **9**, 36.
- J. Cui, J. Liu, H. Wang, L. Ouyang, D. Sun, M. Zhu and X. Yao, *J. Mater. Chem. A*, 2014, **2**, 9645-9655.
- L. Dan, H. Wang, X. Yang, J. Liu, L. Ouyang and M. Zhu, *ACS Appl. Mater. Interfaces*, 2023, **15**, 30372-30382.
- M. Song, J.-L. Bobet and B. Darriet, *J. Alloys Compd.*, 2002, **340**, 256-262.
- Z. Wang, X. Zhang, Z. Ren, Y. Liu, J. Hu, H. Li, M. Gao, H. Pan and Y. Liu, *J. Mater. Chem. A*, 2019, **7**, 14244-14252.
- M. Tian and C. Shang, *Int. J. Hydrogen Energy*, 2019, **44**, 338-344.
- X. Zeng, L. Cheng, J. Zou, W. Ding, H. Tian and C. Buckley, *J. Appl. Phys.*, 2012, **111**.
- Y. Liu, H. Du, X. Zhang, Y. Yang, M. Gao and H. Pan, *Chem. Commun.*, 2016, **52**, 705-708.
- W. Zhu, S. Panda, C. Lu, Z. Ma, D. Khan, J. Dong, F. Sun, H. Xu, Q. Zhang and J. Zou, *ACS Appl. Mater. Interfaces*, 2020, **12**, 50333-50343.
- H. Liu, C. Lu, X. Wang, L. Xu, X. Huang, X. Wang, H. Ning, Z. Lan and J. Guo, *ACS Appl. Mater. Interfaces*, 2021, **13**, 13235-13247.
- W. Zhu, L. Ren, C. Lu, H. Xu, F. Sun, Z. Ma and J. Zou, *ACS nano*, 2021, **15**, 18494-18504.
- J. A. Bolarin, R. Zou, Z. Li, Z. Zhang and H. Cao, *Appl. Mater. Today*, 2022, **29**, 101570.
- W. Ali, X. Li, Y. Yang, N. Li, B. Huang, C. Wu and S. Ding, *ACS Appl. Mater. Interfaces*, 2023, **15**, 36167-36178.
- Z. Huang, Y. Wang and M. Zhang, *Int. J. Hydrogen Energy*, 2021, **46**, 33176-33185.
- C. Lu, H. Liu, L. Xu, H. Luo, S. He, X. Duan, X. Huang, X. Wang, Z. Lan and J. Guo, *J. Magnesium Alloys*, 2022, **10**, 1051-1065.
- H. Gao, R. Shi, Y. Liu, Y. Zhu, J. Zhang, L. Li and X. Hu, *J. Magnesium Alloys*, 2022, **11**, 3724-3735.
- K. R. G. Lim, M. Shekhirev, B. C. Wyatt, B. Anasori, Y. Gogotsi and Z. W. Seh, *Nat. Synth.*, 2022, **1**, 601-614.
- A. VahidMohammadi, J. Rosen and Y. Gogotsi, *Science*, 2021, **372**, eabf1581.
- V. Kamysbayev, A. S. Filatov, H. Hu, X. Rui, F. Lagunas, D. Wang, R. F. Klie and D. V. Talapin, *Science*, 2020, **369**, 979-983.
- M. Li, J. Lu, K. Luo, Y. Li, K. Chang, K. Chen, J. Zhou, J. Rosen, L. Hultman and P. Eklund, *J. Am. Chem. Soc.*, 2019, **141**, 4730-4737.
- Y. Li, H. Shao, Z. Lin, J. Lu, L. Liu, B. Duployer, P. O. Persson, P. Eklund, L. Hultman and M. Li, *Nat. Mater.*, 2020, **19**, 894-899.
- C. Zhou, D. Wang, F. Lagunas, B. Atterberry, M. Lei, H. Hu, Z. Zhou, A. S. Filatov, D.-e. Jiang, A. J. Rossini, R. F. Klie and D. V. Talapin, *Nat. Chem.*, 2023, **15**, 1722-1729.
- W. Zhou, B. Mei, J. Zhu and X. Hong, *Materials Letters*, 2005, **59**, 131-134.
- D. Wang, C. Zhou, A. S. Filatov, W. Cho, F. Lagunas, M. Wang, S. Vaikuntanathan, C. Liu, R. F. Klie and D. V. Talapin, *Science*, 2023, **379**, 1242-1247.
- P. Joensen, R. Frindt and S. R. Morrison, *Mater. Res. Bull.*, 1986, **21**, 457-461.
- A. Ambrosi, Z. Sofer and M. Pumera, *Small*, 2015, **11**, 605-612.
- X. Zhu, Z. Su, C. Wu, H. Cong, X. Ai, H. Yang and J. Qian, *Nano Lett.*, 2022, **22**, 2956-2963.
- N. S. Norberg, T. S. Arthur, S. J. Fredrick and A. L. Prieto, *J. Am. Chem. Soc.*, 2011, **133**, 10679-10681.
- V. Lomonosov, E. R. Hopper and E. Ringe, *Chem. Commun.*, 2023, **59**, 5603-5606.
- I. Persson, J. Halim, H. Lind, T. W. Hansen, J. B. Wagner, L. Å. Näslund, V. Darakchieva, J. Palisaitis, J. Rosen and P. O. Persson, *Adv. Mater.*, 2019, **31**, 1805472.
- M. Alhabeb, K. Maleski, B. Anasori, P. Lelyukh, L. Clark, S. Sin and Y. Gogotsi, *Chem. Mater.*, 2017, **29**, 7633-7644.
- T. Hu, M. Hu, Z. Li, H. Zhang, C. Zhang, J. Wang and X. Wang, *J. Phys. Chem. A*, 2015, **119**, 12977-12984.
- J. Fernandez and C. Sanchez, *J. Alloys Compd.*, 2002, **340**, 189-198.
- C. Zhou, Z. Z. Fang, R. C. Bowman Jr, Y. Xia, J. Lu, X. Luo and Y. Ren, *J. Phys. Chem. C*, 2015, **119**, 22272-22280.
- P. E. De Jongh, *Nat. Mater.*, 2011, **10**, 265-266.
- M. Dornheim, N. Eigen, G. Barkhordarian, T. Klassen and R. Bormann, *Adv. Eng. Mater.*, 2006, **8**, 377-385.
- X. Yao, Z. Zhu, H. Cheng and G. Lu, *J. Mater. Res.*, 2008, **23**, 336-340.
- C. Zhou, Z. Z. Fang and R. C. Bowman Jr, *J. Phys. Chem. C*, 2015, **119**, 22261-22271.
- S. Kang, T. Ogitsu, S. A. Bonev, T. W. Heo, M. D. Allendorf and B. C. Wood, *ECS Trans.*, 2017, **77**, 81.
- I. Gabis, M. Dobrotvorskiy, E. Evard and A. Voyt, *J. Alloys Compd.*, 2011, **509**, S671-S674.
- N. Takeichi, Y. Sakaida, T. Kiyobayashi and H. T. Takeshita, *Mater. Trans.*, 2014, **55**, 1161-1167.
- A. S. Gangrade, A. A. Varma, N. K. Gor, S. Shrinivasan and S. S. V. Tatiparti, *Phys. Chem. Chem. Phys.*, 2017, **19**, 6677-6687.
- M. Khazaei, A. Ranjbar, M. Arai, T. Sasaki and S. Yunoki, *J. Mater. Chem. C*, 2017, **5**, 2488-2503.
- X. Sang, Y. Xie, M.-W. Lin, M. Alhabeb, K. L. Van Aken, Y. Gogotsi, P. R. Kent, K. Xiao and R. R. Unocic, *ACS nano*, 2016, **10**, 9193-9200.
- M. Pozzo and D. Alfe, *Int. J. Hydrogen Energy*, 2009, **34**, 1922-1930.
- T. Vegge, *Phys. Rev. B*, 2004, **70**, 035412.
- A. J. Du, S. C. Smith, X. D. Yao and G. Q. Lu, *J. Phys. Chem. B*, 2006, **110**, 21747-21750.
- J. Čermák and L. Král, *Acta Mater.*, 2008, **56**, 2677-2686.

- 59 L. F. Wan, E. S. Cho, T. Marangoni, P. Shea, S. Kang, C. Rogers, E. Zaia, R. R. Cloke, B. C. Wood and F. R. Fischer, *Chem. Mater.*, 2019, **31**, 2960-2970.
- 60 K.-J. Jeon, H. R. Moon, A. M. Ruminski, B. Jiang, C. Kisielowski, R. Bardhan and J. J. Urban, *Nat. Mater.*, 2011, **10**, 286-290.
- 61 E. S. Cho, A. M. Ruminski, S. Aloni, Y.-S. Liu, J. Guo and J. J. Urban, *Nat. Commun.*, 2016, **7**, 10804.
- 62 D. J. Han, S. Kim and E. S. Cho, *J. Mater. Chem. A*, 2021, **9**, 9875-9881.
- 63 H. Cho, S. Hyeon, H. Park, J. Kim and E. S. Cho, *ACS Appl. Energy Mater.*, 2020, **3**, 8143-8149.
- 64 Y. Cho, S. Kang, B. C. Wood and E. S. Cho, *ACS Appl. Mater. Interfaces*, 2022, **14**, 20823-20834.
- 65 R. D. Rieke, *Science*, 1989, **246**, 1260-1264.
- 66 K. Shirzad and C. Viney, *Journal of the Royal Society Interface*, 2023, **20**, 20230242.
- 67 Q.-Q. Yan, P. Yin and H.-W. Liang, *ACS Mater. Lett.*, 2021, **3**, 1197-1212.
- 68 I. C. Gerber and P. Serp, *Chem. Rev.*, 2019, **120**, 1250-1349.
- 69 F. De Groot, J. Fuggle, B. Thole and G. Sawatzky, *Phys. Rev. B*, 1990, **41**, 928.
- 70 A. Al-Temimy, K. Prenger, R. Golnak, M. Lounasvuori, M. Naguib and T. Petit, *ACS Appl. Mater. Interfaces*, 2020, **12**, 15087-15094.
- 71 K. Prenger, Y. Sun, K. Ganeshan, A. Al-Temimy, K. Liang, C. Dun, J. J. Urban, J. Xiao, T. Petit and A. C. Van Duin, *ACS Appl. Energy Mater.*, 2022, **5**, 9373-9382.
- 72 A. Al-Temimy, B. Anasori, K. A. Mazzio, F. Kronast, M. Seredych, N. Kurra, M.-A. Mawass, S. Raoux, Y. Gogotsi and T. Petit, *J. Phys. Chem. C*, 2020, **124**, 5079-5086.
- 73 P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, **136**, B864.
- 74 W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, **140**, A1133.
- 75 W. Tang, E. Sanville and G. Henkelman, *Journal of Physics: Condensed Matter*, 2009, **21**, 084204.
- 76 E. Sanville, S. D. Kenny, R. Smith and G. Henkelman, *Journal of computational chemistry*, 2007, **28**, 899-908.
- 77 G. Henkelman, A. Arnaldsson and H. Jónsson, *Computational Materials Science*, 2006, **36**, 354-360.
- 78 M. Yu and D. R. Trinkle, *The Journal of Chemical Physics*, 2011, **134**.



Department of Chemical and
Biomolecular Engineering

July 02, 2024

Editor, *Journal of Materials Chemistry A*

Title: Interfacial Charge Transfer Driven by Surface Termination-Controlled Ti₂C MXene for Enhanced Hydrogen Storage in Magnesium

Authors: Min Gyu Kim, ShinYoung Kang, Brandon C. Wood, and Eun Seon Cho

Data Availability Statement

The authors confirm that the data underlying this article are available within the article and its Electronic Supplementary Information (ESI).



KOREA ADVANCED INSTITUTE OF SCIENCE AND TECHNOLOGY

291 DAEHAK-RO, YUSEONG-GU | DAEJEON 34141 | REPUBLIC OF KOREA | TEL: +82-42-350-3912