Energy storage properties of selectively functionalized Cr-group MXenes

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A B S T R A C T

Two-dimensional Cr-group MXene (denoted M_2CT_2, where M represents a Cr group transition metal, and T means none or O/F functionalization) materials sometimes have intrinsic magnetism and metallicity. Using first-principles calculations, the properties of Cr-group MXenes are explored using atom-scale analyses. It is concluded that Cr_2CT_2 compounds are more stable when spin polarized depending on the case, while Mo_2CT_2 and W_2CT_2 are always most stable without magnetism. Besides structural stability, our simulations also predict charge transfer, metallicities, battery performances (capacity, charge-discharge velocity), and thermoelectric properties of Cr-group MXenes. Surprisingly, Cr-group MXenes have superior natures to other popular energy storage materials. Meanwhile, Cr-based MXene (Cr_2CT_2) has unique advantages such as excellent performance with lightest weight. Our results provide insight into MXene cognate research.

1. Introduction

In the face of fossil fuel energy depletion, outstanding alternatives must be put forward to meet the ever-increasing demand for high energy storage density [1,2]. Energy storage materials are always the focus of frontier energy research. Portable devices such as batteries and capacitors occupy dominant research statuses, and their performances mainly depend on efficient ion intercalation in layered materials. MXene has been of great interest in recent studies on energy storage materials [3–9], photonic applications [10,11], adsorbents [12,13], and quantum materials [14,15], which also attracts our attention. Portability and energy efficiency may lead to MXenes being embraced as next-generation energy materials applied to lithium-ion batteries (LIBs) [16,17].

MXenes originate from various solid MAXs consisting of alternately stacked M, A, and X atomic layers [18], where M is an early transition metal, A mostly represents a group 13 or 14 element, X can be carbon and/or nitrogen, and *n* is usually 1, 2, or 3 [19]. The M−X bond is stronger than the M−A one; thus, it is feasible to remove the A atomic layer from the MAX [20,21]. Multilayered MXenes possess conductivities comparable to those of multilayered graphene [22]. Some simulations have uncovered that apart from metallic MXenes, their semiconducting counterparts usually have high Seebeck coefficients (> 100 μV/K at 400 K) near band edges [23,24]. Such high coefficients play an important role in thermoelectric-based solid-state energy conversion devices.

In this work, we uncovered changes in various properties of MXenes composed of different metallic elements of the same group. The information herein will provide a distinct direction for designing specialized energy materials and will reduce aimless MXene investigation. Three Cr-group carbide MXenes (usually performing better than nitrides) represented by M_2CT_2 (M = Cr, Mo, or W; T can be O, F, or no functionalization) were chosen in this study mainly because there have been few experimental or simulation studies on this group to date and because the only chemically characterized one thus far (Mo_2CT_x) has shown superior capacitance ($700F/cm^3$ in 1 M sulfuric acid) and capacity retention (at least 10,000 cycles at 10 A/g) [25]. It can be theoretically predicted that Cr_2CT_x and W_2CT_x may show equally beneficial properties.

Although Cr_2CT_2 has not been experimentally prepared yet (unlike Mo_2CT_2 and W_2CT_2), some theoretically predicted superior properties such as tunable magnetic and electronic properties, low diffusion barriers, high battery capacities, and high Seebeck coefficients as well as theoretical structural stability, as determined from phonon spectra calculations, have still prompted further investigation [18,26–31].

Although reports regarding systematic analyses of the relationships between various MXene properties and Cr-group metal atomic numbers have not been published yet, this paper will describe our studies in detail, which will guide further studies of MXenes composed of other-group transition metals and those whose structures show more layers.
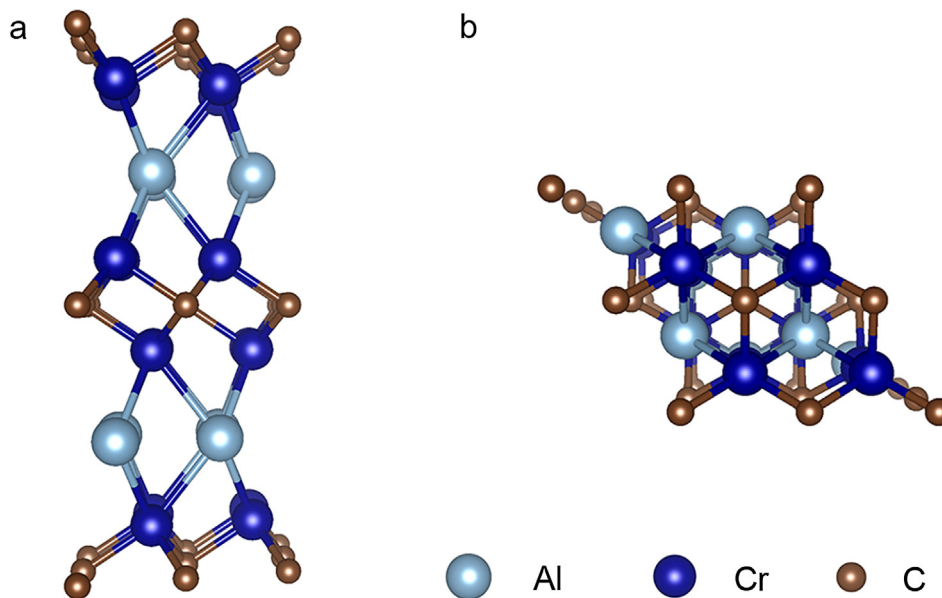
Fig. 1. Original lattice structure of layered MAX $2 \times 2 \times 1$ supercell. (a, b) Side and top views of Cr_2AlC representative model, respectively. Al can represent almost any element of groups 13 and 14, Cr can denote one or diversified early transition metals, and C specifies C and/or N.

2. Computational details

2.1. Original structure models

A $2 \times 2 \times 1$ Cr_2AlC supercell model is presented in Fig. 1. Mo_2AlC and W_2AlC structures, MXene precursor phases in our simulations, are displayed in Fig. S1.

2.2. Methodology

Density functional theory (DFT) was used for all the first-principles calculations, and the ion–electron interactions were described using the projected augmented wave (PAW) method in the Vienna *ab initio* simulation package (VASP) [32–34]. The Perdew–Burke–Ernzerhof (PBE) version of the generalized gradient approximation (GGA) was implemented for the exchange-correlation energy [35]. The Grimme zero-damping DFT-D3 method—an approximate van der Waals (vdW) correction method—was adopted in all the simulations to correctly describe dynamic-correlation-induced vdW interactions [36]. A 550-eV cutoff was sufficient to guarantee convergence of the total energies within 1 meV per atom in the $2 \times 2 \times 1$ MAX and a 500-eV cutoff for the obtained MXene monolayer. Geometry was optimized by the conjugated gradient method; all the atoms were allowed to move until the forces acting on them were < 0.005 eV/Å and the energy converged to within 10^{-6} eV. The Brillouin zone (BZ) was integrated using Monkhorst–Pack (MP) k-point grids of $6 \times 6 \times 2$ for MAX compounds and $7 \times 7 \times 1$ for MXenes during structural relaxation [37], while denser $21 \times 21 \times 1$ and $41 \times 41 \times 1$ MP meshes were used for electronic structure and thermoelectric property calculations, respectively. To prevent interactions introduced by periodic boundary conditions, the vacuum space between two MXene monolayers was 30 Å.

Thermoelectric conversion efficiency usually can be benchmarked with the dimensionless time-dependent figure of merit, $ZT = S^2 \sigma T / (\kappa_e + \kappa_l)$, where S is the Seebeck coefficient, σ the electrical conductivity, T the temperature, and κ_e and κ_l the electronic and lattice contributions to thermal conductivity, respectively. The electronic thermal conductivity can be represented as $\kappa_e = L\sigma T$, where L is the Lorenz number. Based on approximation, the Seebeck coefficient, electrical conductivity and lattice thermal conductivity can be calculated as

$$\sigma_{\alpha\beta}(T,u) = \frac{1}{\Omega} \int \overline{\sigma}_{\alpha\beta}(\varepsilon) \left[-\frac{\partial f(T,\varepsilon,\mu)}{\partial \varepsilon} \right] d\varepsilon \tag{1}$$

$$S_{\alpha\beta}(T,u) = \frac{1}{eT\Omega\sigma_{\alpha\beta}(T,\mu)} \int \overline{\sigma}_{\alpha\beta}(\varepsilon)(\varepsilon-\mu) \left[-\frac{\partial D(T,\varepsilon,\mu)}{\partial \varepsilon} \right] d\varepsilon \tag{2}$$

$$\overline{\sigma}_{\alpha\beta}(\varepsilon) = \frac{e^2}{N} \sum_{i,\mathbf{k}} \tau \nu_\alpha(i,\mathbf{k})\nu_\beta(i,\mathbf{k})\delta(\varepsilon-\varepsilon_{i,\mathbf{k}}) \tag{3}$$

$$k_1^{\alpha\beta} = \frac{1}{k_B T^2 \Omega N} \sum_\lambda f_0(f_0 + 1)(\hbar\omega_\lambda)^2 \nu_\lambda^\alpha F_\lambda^\beta \tag{4}$$

where α and β are tensor indices, Ω is the volume of the unit cell, μ is the chemical potential, D is the Fermi-Dirac distribution function, e and N are the electron charge and the number of k points sampled, ν is the group velocity, k_B is the Boltzmann constant, λ is the phonon mode, f_0 is the equilibrium phonon distribution function, $\hbar$ is the reduced Plank constant, ω_λ is the angular frequency, and F_λ is the mean free displacement.

The first three formulations have been implemented in the Boltzmann Transport Properties package (BoltzTraP code), which is built based on the Boltzmann theory for semi-classical calculations of transport coefficients [38–40]. And the last one can be calculated with ShengBTE [41,42]. Usually the thermoelectric potential of materials can be evaluated by power factor ($S^2\sigma$), and thus MXene unit cells were simulated to get their Seebeck coefficient in this work. Although Seebeck coefficient is not the exclusive factor, high coefficients can obviously obtain considerable thermoelectric potential.

3. Results and discussion

3.1. MXene single layers

By extracting Al layers from MAX phases (lattice constants and total energies are displayed in Table S1), multilayered MXenes showing loosely stacked structures separated by vacant Al layers were obtained. Then, multilayered structures were easily exfoliated into two-dimensional monolayer units consisting of one C layer sandwiched between two M layers forming an edge-shared M_6C octahedral structure. Figs. 2 and S2 show Cr_2C, Mo_2C, and W_2C structures, respectively. The geometry-optimized Cr_2C, Mo_2C, and W_2C lattice constants were