Angewandte Chemie

Supporting Information

Advancing MXene Electrocatalysts for Energy Conversion Reactions: Surface, Stoichiometry, and Stability

C. Tsounis*, P. V. Kumar, H. Masood, R. P. Kulkarni, G. S. Gautam, C. R. Müller, R. Amal, D. A. Kuznetsov*

Table of Contents

Experimental Procedures

Density Functional Theory (DFT) Calculations

(i) For the Mo_2CT_x:Fe system and nitrogen reduction reaction energetics

Calculations were carried out using the GPAW code[1,2] and the structural optimizers in atomic simulation environment (ASE)[3]. The core electrons were treated using the projector augmented wave (PAW) potentials[4], and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional[5] was employed. We performed spin-polarized, gamma-point calculations using a grid spacing of 0.2 Å and an electronic temperature of k_BT = 0.1 eV. All total energies were extrapolated to T = 0 K, and structures were relaxed until residual forces were below 0.05 eV/Å. A 4 × 4 × 1 supercell was used to represent each structure with a vacuum region greater than 10 Å in the *z*-direction.

The free energy changes were computed using the computational hydrogen electrode (CHE) approach[6] where the free energy of $(H^+ + e^-)$ equals 1/2 $H_{2(g)}$ for a standard hydrogen electrode (SHE). The free energy values computed included both the zero-point energy as well as the entropy correction terms. **Table S1** shows the values used for these corrections, which were compiled from literature.[7, 8]

Table S1. Zero-point energy (ZPE) and entropic (TS) correction terms used in this work.

Species	ZPE (eV)	TS (eV)
N_2	0.21	-0.59
H_2	0.34	-0.40
NH_3	0.96	-0.60
*N_2	0.18	-0.03
*N_2H	0.48	-0.06
*N_2H_2	0.80	-0.07
*N	0.08	-0.02
*NH	0.40	-0.03
*NH_2	0.71	-0.04
*NHNH	0.78	-0.09
*$NHNH_2$	1.17	-0.15

(ii) For other calculations

Structural relaxations using DFT[9] were undertaken using a plane-wave basis as implemented in the Vienna Ab-initio Simulations Package (VASP) package until all residual forces acting on each system were less than |0.03| eV/Å[10,11]. The PBE exchange-correlation functional was used with the PAW potentials[12,5]. Each 4 × 4 × 1 MXene slab was separated by at least 10 Å in the *z*-direction unless specified otherwise, and sampled using a gamma-centred *k*-point grid. The hydrogen adsorption energy, ΔE_H, was calculated using the equation:

$$\Delta E_H = E_{system+H} - E_{system} - \frac{1}{2}E_{H_2}$$

where E_H is the hydrogen adsorption energy, $E_{system+H}$ is the energy of the system with an adsorbed proton, E_{system} is the energy of the system without the adsorbed proton, and E_{H_2} is the energy of a hydrogen molecule in the gas phase. The Gibbs free energy of hydrogen adsorption, ΔG_H, was then calculated using the equation:

$$\Delta G_H = \Delta E_H + 0.37\ eV$$

where 0.37 eV is used to account for changes in the zero-point energy and entropy between hydrogen in the gas phase and the adsorbed state on the MXene slab.[13]

Pourbaix Diagrams

Pourbaix diagrams were generated using pymatgen,[14] by considering all competing ionic and molecular species that may form in solution with the MXene solid from the Materials Project database.[15] The energies of the aqueous ionic and molecular species were taken from literature,[16] while the energies of the MXene solid itself were estimated using DFT as described above. The DFT calculations were performed using the convergence parameters in MPRelaxSet of pymatgen, which ensured compatibility with data from the Materials Project database.

The thermodynamic variable used to construct the Pourbaix diagram is the Gibbs free energy of formation. The Gibbs free energy of formation, G_i, of each species i in the solution can be determined as:

$$G_i(c_i, pH, \emptyset) = G_i° + 0.0591 \log_{10} c_i - n_O \mu_{H_2O} + pH(n_H - 2n_O) + \emptyset(-n_H + 2n_O + q_i)$$

where $G_i°$ is the standard Gibbs free energy of formation of the species, c_i is its concentration, n_O and n_H are the respective numbers of oxygen and hydrogen atoms in the species, μ_{H_2O} is set to the energy of formation of water at −2.46 eV, $\emptyset$ is the electric potential, and q_i is the species' charge. For our diagrams, we chose a moderate concentration of 10^{-3} M for all ionic species in the medium, under standard conditions of temperature and pressure. The Pourbaix diagram shows the species whose Gibbs free energy of formation is less than or equal to zero at the given conditions of $\emptyset$ and pH, *i.e.*, the convex hull of the species in the aqueous medium. The relative stability of the MXene solid (indicated by the color bar in **Figure 5** of the main text) is plotted by taking the difference between the convex hull and the MXene's Gibbs free energies of formation at those conditions. The colored dashed lines in **Figure 5** of the main text show the variation of the reduction potential with $\emptyset$ and pH for a few common species;[17] these reduction potentials can be used as estimates for the stability region of water (red lines), carbon dioxide (green line), and nitrogen (blue line) in aqueous medium.

The linear correction scheme by Persson *et al.*[18] was used to compare the data from various sources and account for the difference between the experimental and DFT calculated formation energies. In this scheme, the experimental chemical potential of an ion or molecule is shifted by the difference between the DFT and experimentally obtained energies of formation for a reference compound. The reference compound is usually a binary oxide containing the same element as the ion. The corrected chemical potential of an aqueous ion or molecule, $\mu_i°_{(aq)}$, can be written as:

$$\mu_{i\,(aq)}^0 = \mu_{i\,(aq)}^{0,\,exp} + \left[\Delta g_s^{0,DFT} - \Delta g_s^{0,exp}\right] = \mu_{i\,(aq)}^{0,exp} + \Delta \mu_s^{0,DFT-exp}$$

Here, $\mu_{i(aq)}^{0,exp}$ is the experimentally obtained chemical potential of the species i, $\Delta g_s^{0,DFT}$ is the Gibbs free energy of formation calculated using DFT and $\Delta g_s^{0,exp}$ is the experimentally obtained Gibbs free energy of formation for the reference compound. In our diagram, we added the correction to all the atoms in the ion or molecule using pymatgen before determining the Pourbaix diagram, which ensured an accurate comparison between DFT and experimentally obtained formation energies.

Supporting Results

Table S1. Calculated Gibbs free energy of hydrogen adsorption for high entropy MXenes at different adsorption sites.

MXene Structure	ΔG_H / eV
TiVNbMoC$_3$O$_4$ site 2	-0.51
TiVNbMoC$_3$O$_4$ site 3	-0.50

References

[1]   J.J. Mortensen, L. B. Hansen, K. W. Jacobsen, *Phys. Rev. B* **2005**, *71*, 035109.

[2]   J. Enkovaara, C. Rostgaard, J. J. Mortensen, J. Chen, M. Dułak, L. Ferrighi, J. Gavnholt, C. Glinsvad, V. Haikola, H. A. Hansen, H. H. Kristoffersen, M. Kuisma, A. H. Larsen, L. Lehtovaara, M. Ljungberg, O. Lopez-Acevedo, P. G. Moses, J. Ojanen, T. Olsen, V. Petzold, *et al., J. Phys. Condens. Matter* **2010**, *22*, 253202.

[3]   A. H. Larsen, J. J. Mortensen, J. Blomqvist, I. E. Castelli, R. Christensen, M. Dułak, J. Friis, M. N. Groves, B. Hammer, C. Hargus, E. D. Hermes, P. C. Jennings, P. B. Jensen, J. Kermode, J. R. Kitchin, E. L. Kolsbjerg, J. Kubal, K. Kaasbjerg, S. Lysgaard, J. B. Maronsson, *et al.*, *J. Phys. Condens. Matter* **2017**, *29*, 273002.

[4]   P. E Blöchl, *Phys. Rev. B* **1994**, *50*, 17953−17979.

[5]   J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

[6]   A. A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl, J. K. Nørskov, *Energy Environ. Sci.* **2010**, *3*, 1311.

[7]   J. G. Howalt, T. Bligaard, J. Rossmeisl, T. Vegge, *Phys. Chem. Chem. Phys.* **2013**, *15*, 7785-7795

[8]   X. Ren, J. Zhao, Q. Wei, Y. Ma, H. Guo, Q. Liu, Y. Wang, G. Cui, A. M. Asiri, B. Li, B. Tang, X. Sun, *ACS Cent. Sci.* **2019**, *5*, 116-121

[9]   W. Kohn, L. J. Sham, *Phys. Rev.* **1965**, *140*, A1133.

[10]   G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169–11186.

[11]   G. Kresse, J. Furthmüller, *Comput. Mater. Sci.* **1996**, *6*, 15–50.

[12]   G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, *59*, 1758–1775.

[13]   C. Ling, L. Shi, Y. Ouyang, Q. Chen, J. Wang, *Adv. Sci.* **2016**, *3*, 1600180.

[14]   S. P. Ong, W. D. Richards, A. Jain, G. Hautier, M. Kocher, S. Cholia, D. Gunter, V. L. Chevrier, K. A. Persson, G. Ceder, *Comput. Mater. Sci.* **2013**, *68*, 314–319.

[15]   A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K. A. Persson, *APL Mater.* **2013**, *1*, 011002.

[16]   J. W. Johnson, E. H. Oelkers, H. C. Helgeson, *Comput. and Geosci.* **1992**, *18*, 899–947.

[17]   P. Vanýsek, *CRC Handbook of Chemistry and Physics, 89th Edition*, Marcel Dekker, **1978**.

[18]   K. A. Persson, B. Waldwick, P. Lazic, G. Ceder, *Phys. Rev. B* **2012**, *85*, 235438.