Published by
NIGERIAN SOCIETY OF PHYSICAL SCIENCES
Available online @ https://asr.nsps.org.ng/index.php/asr

African Scientific Reports 2 (2023) 88

African Scientific Reports

Screening of Metal-Ion Intercalated Yttrium Carbide and Nitride MXenes for Energy Storage Applications via Density Functional Theory

E. Omugbe[a,b,*], O.E. Osafile[b], N. O. Nenuwe[b], E. A. Enaibe[b]

[a] *Department of Physics, University of Agriculture and Environmental Sciences, Umuagwo, Imo State, Nigeria*
[b] *Department of physics, Federal University of Petroleum Resources, 330102, Effurun, Delta State, Nigeria.*

Abstract

Rechargeable batteries and energy storage devices play a major role in many facets of human endeavour due to their efficiency and portability. In this work, we investigated the suitability of single-layer intercalated Yttrium-based MXenes Y_2CT_2 (T= Li, Mg, Al) and Y_2NLi_2 as potential energy storage materials using the first principle calculation within the framework of the density functional theory approach. Upon intercalation, the lattice constants of the MXenes expand due to the size of the intercalating species and the electrostatic repulsion. We obtained the theoretical gravimetric capacities, open circuit voltages and adsorption energies. The obtained open circuit voltages for Y_2CT_2 (T= Li, Mg) and Y_2NLi_2 falls within the voltage window of $0-1.0V$ which has been found to eliminate dendrites formation caused by alkaline metals during the discharge-charge cycle. The adsorption energies indicate the stability of the intercalating ion on the MXenes surfaces except for Al cation. The results are consistent with other studies on similar MXene families in the existing literature. The work may aid the understanding of the electrochemical properties of 2D materials and we recommend Y_2CLi_2, Y_2NLi_2, and Y_2CMg_2 for future investigation as potential materials for rechargeable batteries.

DOI:10.46481/asr.2023.2.1.88

Keywords: Energy storage materials, Lithium-ion batteries, Magnesium-ion batteries, Rechargeable batteries, 2D MXene materials.

Article History :
Received: 28 January 2023
Received in revised form: 03 April 2023
Accepted for publication: 04 April 2023
Published: 24 April 2023

Communicated by: Wasiu Yahya

*Corresponding author tel. no:+234 7068580051
Email address: omugbeekwevugbe@gmail.com (E. Omugbe)

1. Introduction

Electrochemical energy storage materials applications have grabbed the curiosity of many researchers and commercial companies in recent years given their advantages over fossil fuels. Generally, energy storage devices may be employed in many applications such as rechargeable batteries, phones, laptops, wrist watches, powering automobiles and so on. Owing to their efficiency and portability, efforts have been put into research to determine and synthesize suitable and low-cost materials for energy storage device applications. The methods employed in determining the energy storage materials are experimental and theoretical techniques. A theoretical method such as the first principle approach [1–4] has been used to simulate the electronic structure, mechanical properties [5, 6], thermoelectric properties [7–9] energy storage [10–17] and others. This method has been implemented into various computing codes such as VASP [18], CASTEP [19], QUANTUM ESPRESSO [20, 21], WEIN2K [22] and so on. The codes offer the advantage of being low-cost and can be used to simulate the artificial properties of materials. Such simulation results may be compared to experimental data and also help the experimentalist in making decisions during the fabrication process. Materials for energy storage have drawn the attention of the material science community in recent decades. To this end, two-dimensional (2D) materials such as Graphene [23, 24] and MXenes [10, 11, 25] have been explored due to their unique quality in retaining electrochemical energy.

The MXenes family belongs to a large group of 2D systems due to the combination of different chemical elements and structural arrangements. The MXenes possess chemical formula $M_{n+1}X_nT_2$ and are derived from the 3D parent ternary compounds known as MAX phases ($M_{n+1}\mathrm{AX}_nT_2$) through acid (HCl and HF or both) etching of the A elements [10]. The respective elements M, A, X and T represent early transition metals (Ti, Ta, Nb, Y, W, Sc, V, Mo Zr), group 13 or 14 elements, Carbon and or Nitrogen and surface termination groups. The chemical acid synthesis has Oxygen (O), Fluorine (F) and hydroxyl elements as the as-prepared functional groups. Other surface groups (FH, H, Br, ClH and so on) have been derived [26] and found to be chemically stable on the bare MXenes. A few double transition metal MXenes have been synthesized [27–29] with many others predicted theoretically [30–34]. The structural configurations and wide range of chemical elements make the MXenes material a large family of 2D materials comparable to the Perovskites, metal oxides/hydroxides, transition metal dichalcogenides, graphene and its derivatives [35]. The structural arrangements, the nature of the transition metals and surface terminations elements give rise to different electronic structures such as metallic, semi-metallic, semiconductor, insulator and magnetic ordering. These properties have been explored in electrochemical energy storage [10, 11], thermoelectric applications [26, 36–42], water purification [43–45], triboelectric devices [46], sensors [47–50] and telecommunications [51]. The most relevant application to our work is in energy storage where many authors have explored using both theoretical and experimental methods [52–60].

The motivation in this current work is two-fold. (a) To use the density functional theory (DFT) approach to predict potential energy storage properties for new MXene systems as alternatives to existing materials. (b) In a recent work [25], the screening of many MXenes materials for potential energy storage applications has been investigated theoretically. However, we are proposing new MXenes not included in [25]. We studied the theoretical gravimetric capacity and open-circuit voltage of mono-layer Y_2CLi_2, Y_2NLi_2, Y_2CMg_2 and Y_2CAl_2 MXenes using the DFT approach. The organization of the remaining part of the paper is as follows: in section two, we will present the theoretical method of computation. Section three contains the discussion of the results and in section four we will give the conclusion.

2. Materials and Method

We considered the screening of mono-layer MXenes materials for battery applications by intercalating metal ions such as Li^+ Mg^{2+} Al^{3+} into the MXene layers using first principles calculation within the framework of the DFT approach. We used Yttrium-based MXenes as case studies. In particular, the following MXenes Y_2CT_2 (T= Li, Mg, Al) and Y_2NLi_2 are treated with the augmented plane wave method as implemented in the QUANTUM ESPRESSO package [15, 16]. For the structural optimization, we used a $12 \times 12 \times 1$ Monkhorst and Pack [61] k points grids for the Brillouin zones integration. We employed the generalized gradient approximation (GGA) of Perdew Burke and Ernzenhof (PBE) for the exchange-correlation functional [62] and utilized a plane-wave cutoff kinetic energy of

105Ry for the wave function. Furthermore, we used a cutoff of 630Ry for the charge density and potential. The total energy convergence threshold was set at 1×10^{-10}Ry. We used the Methfessel-Paxton smearing scheme [63] with a smearing width of 0.011Ry. As for the bare MXenes, we used $10 \times 10 \times 1$ Monkhorst and Pack k points grids to sample the Brillouin zones. The plane-wave cutoff kinetic energy of 80Ry and a cutoff of 480Ry were used for the wave function and the charge density respectively. The density of state calculations was obtained using a $30 \times 30 \times 1$ k-points grid with the tetrahedron method [64]. To circumvent any interaction between a monolayer and its periodic images we set a vacuum space of 20 Å along the c axis. The 2D MXenes possess a hexagonal crystal structure with symmetry P-3m1 and space group number 164. The symmetry points for the Brillouin zone are $\Gamma\,(0,0,0)$, M(1/2, 0,0) and $K\left(\frac{1}{3},\frac{1}{3},0\right)$. The structure of the bare MXene before and after metal ion intercalation is presented in Figure 1. The relaxed atomic positions were then used to calculate the total energies of the intercalated and bare MXenes. The chemical potential of the intercalating ion was also determined. We calculated the quantities such as the theoretical gravimetric capacity, adsorption energies and the open circuit voltages (OCV). Using M as an intercalant, we can represent the following general chemical reaction as

$$Y_2C + 2M \rightarrow Y_2\mathrm{CM}_2. \tag{1}$$

The adsorption energy of intercalated species can be obtained as

$$E_{\mathrm{ad}} = E\,[Y_2\mathrm{CM}_2] - E\,[Y_2C] - 2\mu\,[M] \tag{2}$$

where $E\,[Y_2C]$, $E\,[Y_2\mathrm{CM}_2]$ and $\mu\,[M]$ are the respective total energies of pristine, intercalated MXene and the chemical potential of the intercalants.

The theoretical gravimetric capacity and OCV are given by the respective equations [25, 65]

$$Q_g = \frac{\mathrm{xnF}}{m} \tag{3}$$

$$V = \frac{E\,[Y_2C] + x\mu\,[M] - E\,[Y_2\mathrm{CM}_2]}{xne} \tag{4}$$

where n represents the valence state of fully ionized cations from the electrolyte [65], specifically, $n = 1$ for Li, $n = 2$ for Mg and $n = 3$ for Al. We used the concentration ($x = 2$) for the intercalated MXenes monolayers. In equation (3), F, e and M represent the Faraday constant ($26801\mathrm{mA}hg^{-1}$) electronic charge and the molar mass or chemical weight of the intercalated MXene sheets.

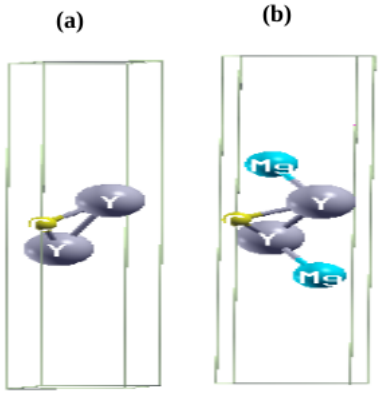

Figure 1. (a) Mono-layer of bare Yttrium carbide MXene (Y_2C) (b) Intercalation of Yttrium carbide MXene with Mg-ion (Y_2CMg_2).

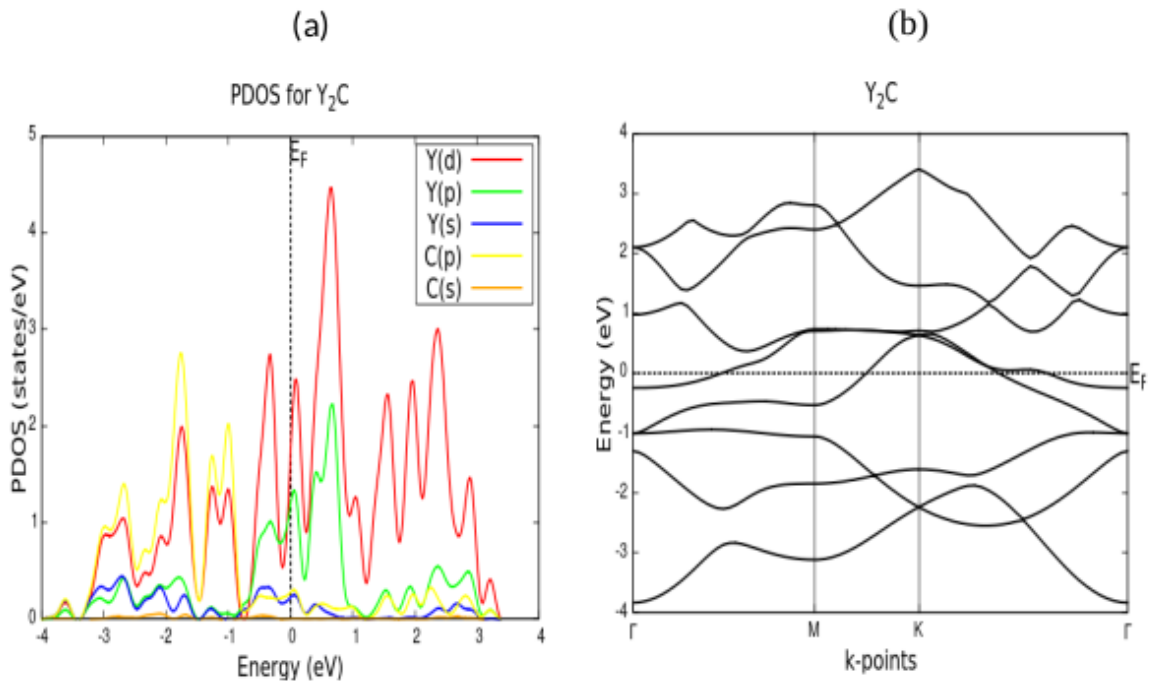

Figure 2. (a) Projected density of states. (b). Energy band diagram of bare Y_2N.

Table 1. Open circuit voltage, adsorption energy and theoretical gravimetric capacity of intercalated Yttrium carbide/nitride-based MXenes

MXene	Open circuit Voltage(V)	Theoretical gravimetric Capacity (mAh/g)	Adsorption energy (eV)
Y_2CLi_2	0.06	263.138	-0.12
Y_2NLi_2	0.08	260.585	-0.16
Y_2CMg_2	0.02	449.619	-0.07
Y_2CAl_2	-0.43	659.909	2.60

3. Results and Discussion

The lattice parameter of the bare MXenes changes when metal ions are diffused into their surfaces. For the bare MXene Y_2C, the lattice parameter is found as 3.60A. After intercalation with Mg, Al and Li ions, the lattice constants expand by 19.44% for Y_2CMg_2, 13.89% for Y_2CAl_2 and Y_2CLi_2. The changes in the lattice parameters have been linked to the ionic radius of intercalating species and lateral electrostatic repulsion after ion intercalations [25]. The bare MXenes Y_2C (see Ref [26]) and Y_2N (see Figure 2) are metallic with the 3d electrons of Y-atom majorly contributing to electrical conductivity. The metallic nature of the bare MXenes indicates that they have an intrinsic advantage for high-performance electrode materials [65]. In Table 1, we presented the theoretical gravimetric capacities, open circuit voltages and adsorption energies for the Y_2CLi_2, Y_2NLi_2, Y_2CMg_2 and Y_2CAl_2 MXenes with Al and Mg intercalated MXenes having the highest values of 659.909mAh/g and 449.319mAh/g respectively. The high values compared to the lithiated MXenes can be attributed to the multivalence states of the Mg and Al ions. The theoretical gravimetric capacity of Y_2CLi_2 MXene is slightly higher than that of Y_2NLi_2 due to its lighter molar weight. The respective OCVs and the adsorption energies are positive and negative for Y_2CLi_2, Y_2NLi_2, Y_2CMg_2 which may be an indication of a favourable condition for battery applications. The nitride-based MXene has a higher OCV than the corresponding carbide MXene due to the extra electron of the nitrogen atom and higher adsorption energy. For the Y_2CAl_2 MXene, the respective OCV and adsorption energy is negative and positive making the MXene system unsuitable for energy storage application. Generally, the OCVs increase with a decrease in the theoretical gravimetric capacities for all MXenes. Also, the intercalated bare MXenes have been found in [25] to have open

circuit voltage characteristics of $0 - 1.0V$ which is consistent with the present results. This low voltage window has been found to prevent dendrite formation by alkaline metals during the discharge and charge processes [65, 66].

4. Conclusion

We have presented a study on the screening of intercalated bare MXenes for possible application in metal ion batteries. We used the DFT method to determine the total energies of the MXenes Y_2C and Y_2N, Y_2CLi_2, Y_2NLi_2, Y_2CMg_2 and Y_2CAl_2. The bare MXenes are metallic which allows their usage for high-performance electrode materials. We found a linear correlation between the calculated theoretical gravimetric capacities and the OCVs. The obtained OCV falls within the range of $0 - 1.0V$ which have been reported to eliminate dendrite formation by alkaline metals during the discharge and charge process. The results revealed that the metal ion and the X sites of the MXene materials is responsible for the OCV characteristics. Furthermore, our results are consistent with the works reported in existing literature [25, 65] where the authors studied similar MXene materials. These findings may contribute to the understanding of electrochemical properties of 2D material and we recommend Y_2CLi_2, Y_2NLi_2, and Y_2CMg_2 for future investigation as potential materials for rechargeable batteries.

References

[1] N.M. Caffrey, "Prediction of Optimal Synthesis Conditions for the Formation of Ordered Double-Transition-Metal MXenes (o-MXenes)", J. Phys. Chem. C **124** (2020) 18797

[2] H. Wang, Z. Jing,, H. Liu, X. Feng, G. Meng, K. Wu, Y. Cheng & B. Xiao, "A high throughput assessment of the adsorption capacity and Li-ion diffusion dynamics in Mo-based ordered double-transition-metal MXenes as anode materials for fast-charging LIBs", Nanoscale **12** (2020) 24510.

[3] T.B. Martins, R.H. Miwa, A.J. Da Silva & A. Fazzio, "Electronic and transport properties of boron-doped graphene nanoribbons", Phys. Rev. Lett. **98** (2007) 196803,

[4] M. Kurtoglu, M. Naguib, Y. Gogotsi & M.W. Barsoum, "First principles study of two-dimensional early transition metal carbides", MRS Communications, **2** (2012) 133.

[5] A. Lipatov, H. Lu, M. Alhabeb, B. Anasori, A. Gruverman, A. Sinitskii & Y. Gogotsi, "Elastic properties of 2D $Ti_3C_2T_x$ MXene monolayers and bilayers", Sci. Adv. **4** (2018) eaat0491.

[6] V.N. Borysiuk, V.N. Mochalin & Y. Gogotsi, "Molecular dynamic study of the mechanical properties of two - dimensional titanium carbides $Ti_{n+1}C_n$ (MXenes)", Nanotechnology, **26** (2015) 265705.

[7] B.U. Haq, S. Alfaify, T. Alshahrani, R. Ahmed, Q. Mahmood, D.M. Hoat & S. A. Tahir, "Investigation of thermoelectric properties of ZnO monolayers from firstprinciple approach", Phys. E Low-dimens. Syst. Nanostruct **136** (2021) 114444.

[8] B.U. Haq, S. Alfaify & A. Laref, "Design and characteristic of novel polymorphs of single-layered tin-sulfide for direction dependent thermoelectric applications using first-principles approaches", Phys. Chem. Chem. Phys. **21** (2019) 4624.

[9] B.U. Haq, S. Alfaify & A. Laref, "Exploring novel flat band polymorphs of singlelayered Germanium Sulfide for high-efficiency thermoelectric application", J. Phys. Chem. C **123** (2019) 18124.

[10] M. Naguib, J. Halim, J. Lu, M. K. Cook, L. Hultman, Y. Gogotsi & M.W. Barsoum, "New two-dimensional Niobium and vanadium carbides as promising materials for Li-ion batteries", J. Am. Chem. Soc. **135** (2013) 15966.

[11] H. Tang, Q. Hu, M. Zheng, Y. Chi, X. Qin, H. Pang & Q. Xu, "MXene-2D layer electrode materials for energy storage", Prog. Natl. Mater. Sci. Mater. Int. **28** (2018) 133.

[12] E. E. Elemike, O. E. Osafile & E. Omugbe "New perspectives 2Ds to 3Ds MXenes and graphene functionalized systems as high performance energy storage materials", Journal of Energy Storage **42** (2021) 102993.

[13] M. Saraf, T. Zhang, T. Averianov, C.E. Shuck, R.W. Lord, E. Pomeraritseva & Y. Gogotsi, "Vanadium and Niobium Mxenes-Bilayered V_2O_5 Asymmetric supercapacitors", Small methods **2201551** (2023), https://doi.org/10.1002/smtd.202201551.

[14] Y. Gogotsi, "Monolithic integrated MXene supercapacitors may power future electronics", National Science Review **10** (2023) 20

[15] A. Inman, T. Hryhorchuk, L. Bi, R.J. Wang, B. Greenspan, T. Tabb, E.M. Gallo, A. Vahidmohammadi, G. Dion, A. Danielescu & Y. Gogotsi, "Wearable energy storage with Mxen textile supercapacitors for real world use", J.Mater. Chem. **11** (2023) 3514.

[16] E. Vorobyeva, F. Lissel, M. Salanne, M.R. Lukatskaya, "Bottom up design of configurable oligomer derived conducting metallopolymers for high-power electrochemical energy storage", ACS nano **15** (2021) 15422.

[17] Y. Xie, Y. Dall Agnese, M. Naguib, Y. Gogotsi, M.W. Barsoum, H.L.L. Zhaung & P.R. Kent, "Rediction and characterization of MXene nanosheets. Anodes for non-Li ion batteries", ACS Nano **8** (2014) 9606.

[18] G. Kresse & J. Furthmüller, "Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set", Phys. Rev. B: Condens. Mater. Phys. **54** (1996) 111693.

[19] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson & M. C. Payne, "First principles methods using CASTEP", Zeitschrift fuer Kristallographie **220** (2005) 567.

[20] P. Giannozzi, et al., "Quantum ESPRESSO: a modular and open-source software project for quantum simulations of materials", J. Phys. Condens. Matter **21** (2009) 395502.

[21] P. Giannozzi, et al., "Advanced capabilities for materials modelling with Quantum ESPRESSO", J. Phys. Condens. Matter **29** (2017) 465901.

[22] P. Blaha, K. Schwarz, F. Tran, R. Laskowski, G.K.H. Madsen & L.D. Marks, "WIEN2k: An APW+lo program for calculating the properties of solids" J. Chem. Phys. **152** (2020) 074101.

[23] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva & A.A. Firsov, "Electric field effect in atomically thin carbon films", Science **306** (2004) 666.

[24] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, M.I. Katsnelson, I.V. Grigorieva, S.V. Dubonos & A.A. Firsov, "Two-dimensional gas of massless Dirac fermions in graphene", Nature **438** (2005) 197.

[25] C. Eames & M.S. Islam, "Ion Intercalation into Two-Dimensional Transition-Metal Carbides:Global Screening for New High-Capacity Battery Materials", J. Am. Chem. Soc. **136** (2014) 16270.

[26] E. Omugbe , O.E. Osafile, O.N. Nenuwe & E.A. Enaibe. "Energy band gaps and novel thermoelectric properties of two-dimensional functionalized Yttrium carbides (MXenes)", Physica B **639** (2022) 413922.

[27] R. Syamsai, J.R. Rodriguez, V.G. Pol, V. Q. Le, K. M. Batoo, S.F. Adil, S. Pandiaraj, M.R. Muthumareeswaran, E.H. Raslan & A.N. Grace, "Double transition metal MXene (TixTa4-xC3) 2D materials as anodes for Li-ion batteries", Scientific Reports **11** (2021) 688.

[28] B. Anasori, C. Shi, E.J. Moon, Y. Xie, C.A. Voigt, P. R. C. Kent, D. May, S. J. L. Billinge, M.W. Barsoum & Y. Gogotsi, "Control of electronic properties of 2D carbides (MXenes) by manipulating their transition metal layers", Nanoscale Horiz. **1** (2016) 227.

[29] K. Hantanasirisakul, B. Anasori, S. Nemsak, J.L. Hart, L. Wu, Y. Yang, R.V. Chopdekar, P. Shafer, A.F. May, E.J. Moon, J. Zhou, Q. Zhang, M. L. Taheri, S.J. May & Y. Gogotsi, "Evidence of a magnetic transition in atomically thin Cr2TiC2Tx MXene", Nanoscale Horiz. **5** (2020)1557.

[30] R. Meshkian, Q. Tao, M. Dahlqvist, J. Lu, L. Hultman & J. Rosén, "Theoretical stability and materials synthesis of a chemically ordered MAX phase, Mo2ScAlC2, and its two-dimensional derivate Mo2ScC2 MXene", Acta Materialia **125** (2017) 476.

[31] W.Sun, Y. Xie & P R. C. Kent, "Double transition metal MXenes with wide band gaps and novel magnetic properties", Nanoscale **10** (2018) 11962.

[32] L. Li, "Lattice dynamics and electronic structures of Ti3C2O2 and Mo2TiC2O2 (MXenes): The effect of Mo substitution", Computational Materials Science **124** (2016) 8.

[33] D. Jin, L.R. Johnson, A.S. Raman, X. Ming, Y. Gao, F. Du, Y. Wei, G. Chen, A. Vojvodic, Y. Gogotsi & X. Meng, "Computational Screening of 2D Ordered Double Transition-Metal Carbides (MXenes) as Electrocatalysts for Hydrogen Evolution Reaction", J. Phys. Chem. C **124** (2020) 10584.

[34] J. He, G. Ding, C. Zhong, S. Li, D. Li & G. Zhang, "Cr2TiC2-based double MXenes: novel 2D bipolar antiferromagnetic semiconductor with gate-controllable spin orientation toward antiferromagnetic spintronics", Nanoscale **11** (2019) 356.

[35] A. K. Geim & I.V. Grigorieva, "Van der Waals heterostructures", Nature **499** (2013) 419.

[36] M. Khazaei, M. Arai, T. Sasaki, M. Estili & Y. Sakka, "Two-dimensional molybdenum carbides: potential thermoelectric materials of the MXene family", Phy. Chem.. Chem. Phys. **16** (2014) 7841.

[37] M. Khazaei, M. Arai, T. Sasaki, C.Y. Chung, N.S. Venkataramanan, M. Estili, Y. Sakka & Y. Kawazoe, "Novel electronic and magnetic properties of twodimensional transition metal carbides and nitrides", Adv. Funct. Mater. **23** (2013) 2185.

[38] A.N. Gandi, H.N. Alshareef & U. Schwingenschlogl, "Thermoelectric performance of the MXenes M_2CO_2 (M = Ti, Zr, or Hf)", Chem. Mater. **28** (2016) 1647.

[39] S. Kumar & U. Schwingenschlogl, "Thermoelectric performance of functionalized Sc_2C MXenes", Phys. Rev. B **94** (2016) 035405.

[40] Z. Jing, H. Wang, X. Feng, B. Xiao, Y. Ding, K. Wu & Y. Cheng, "Superior thermoelectric performance of ordered double transition metal MXenes: $Cr_2TiC_2T_2$ (T = - OH or - F)", J. Phys. Chem. Lett. **10** (2019) 5721.

[41] H. Kim, B. Anasori, Y. Gogotsi & H.N. Alshareef, "Thermoelectric properties of two dimensional Molybdenum-based MXenes", Chem. Mater. **29** (2017) 6472.

[42] S. Sarikurt, D. Carkir, M. Keceli & C. Sevik, "Influence of surface functionalization on thermal transport and thermoelectric properties of MXene monolayers", Nanoscale. **10** (2018) 8859.

[43] C.E. Ren, K.B. Hatzell, M. Alhabeb, Z. Ling, K.A. Mahmoud & Y. Gogotsi, "Charge and size ion selective sieving through $Ti_3C_2T_x$ membrane", J. Phys. Chem. Lett. **6** (2015) 4026.

[44] Q. Pang, J.X. Guo, Q.R. Zhang, J.Y. Xiang, B.Z. Liu, A.G. Zhou, R.P. Liu & Y.J. Tian, "Unique Lead adsorption behavior of activated hydroxyl group in two-dimensional Titanium Carbide", J. Am. Chem. Soc. **136** (2014) 4113.

[45] Y. Ying, Y. Liu, X.Y. Wang, Y.Y. Mao & W. Cao, "Two -dimensional Titanium Carbide for efficiently reductive removal of highly toxic Chromium (VI) from water", ACS Appl. Matter. Interfaces **7** (2015) 1795.

[46] Y. Dong, S.S.K. Mallineni, K. Maleski, H. Behlow, V.N. Mochalin, A.M. Rao, Y. Gogotsi & R. Podila, "Metallic MXenes: a new family of materials for flexible triboelectric nanogenerators", Nano Energy **44** (2018) 103.

[47] F. Wang, C.H. Yang, C.Y. Duan, D. Xiao, Y. Tang & J.F. Zhu, "An organ-like Titanium Carbide material (MXene) with multilayer structure encapsulating hemoglobin for a mediator-free biosensor", J. Electrochem. Soc. **162** (2015) B16.

[48] C.B. Hatter, A. Sarycheva, A. Levitt, B. Anasori, L. Nataraj & Y. Gogotsi, "Electrically Conductive MXene-Coated Glass Fibers for Damage Monitoring in Fiber-Reinforced Composites", J. Carbon Res. **6** (2020) 1.

[49] P.A. Rasheed, R.P. Pandey, T. Gomez, K.A. Jabbar, K. Prenger, M. Naguib, B. Aissa & K.A. Mahmoud, "Nb-based MXenes for the efficient electrochemical sensing of small biomolecules in the anodic potential", Electrochem. Commun. **119** (2020) 106811.

[50] S.J. Kim, H.J. Koh, C.E. Ren, O. Kwon, K. Maleski, S.Y. Cho, B. Anasori, C.K. Kim, Y. K. Choi, J. Kim, Y. Gogotsi & H.T. Jung, "Metallic $Ti_3C_2T_x$ MXene gas sensors with ultrahigh signal-to-noise ratio", ACS Nano **12** (2018) 986.

[51] A. Sarycheva, A. Polemi, Y. Liu, K. Dandekar, B. Anasori & Y. Gogotsi, "2D Titanium carbide (Mxene) for wireless communication", *S*ci. Adv. **4** (2018) 1.

[52] R.B. Rakhi, B. Ahmed, M.N. Hedhili, D.H. Anjum & H.N. Alshareef, "Effect of post etch annealing gas composition on the structural and electrochemical properties of Ti_2CT_x MXene Electrodes for Supercapacitor Applications", Chem mater **27** (2015) 5314.

[53] M.R. Lukatskaya, E. Mashtalir, C.E. Ren, Y.D. Agnese, P. Rozier, P.L. Taberna, M. Naguib, P. Simon, M.W. Barsoum & Y. Gogotsi, "Cation Intercalation and High Volumetric Capacitance of Two-Dimensional Titanium Carbide" Science, **341** (2013) 1502.

[54] M. Ghidiu, M.R. Lukatskaya, M. Q. Zhao, Y. Gogotsi & M.W. Barsoum, "Conductive two-dimensional titanium carbide 'clay' with high

volumetric capacitance", Nature. **516** (2014) 78.
[55] J. Halim, S. Kota, M.R. Lukatskaya, M. Naguib, M.Q. Zhoa, E.J. Moon, J. Pitock, J. Nanda, S. J. May & Y. Gogotsi, "Synthesis and characterization of 2D Molybdenum Carbide (MXene)", Adv. Funct. Mater, **26** (2016) 3118.
[56] J. Zhu, A. Chroneos, J. Eppinger & U. Schwingenschlögl, "S-functionalized MXenes as electrode materials for Li-ion batteries", Applied material today **5** (2016) 19.
[57] J. Zhou, X. Zha, X. Zhou, F. Chen, G. Gao, S. Wang, C. Shen, T. Chen, C. Zhi, P. Eklund, S. Du, J. Xue, W. Shi, Z. Chai & Q. Huang, "Synthesis and Electrochemical Properties of Two-Dimensional Hafnium Carbide", ACS Nano **11** (2017) 3841.
[58] M. Naguib, R.R. Unocic, B. L. Armstrong & J. Nanda, "Large-scale delamination of multilayers transition metal carbides and carbonitrides MXenes", Dalton Trans. **4** (2015) 9353.
[59] B. Anasori, Y. Xie, M. Beidaghi, J. Lu, B.C. Hosler, L. Hultman, P.R.C. Kent, Y. Gogotsi, & M.W. Barsoum, "Two- Dimensional, Ordered, Double Transition Metals Carbides (MXenes)", *ACS Nano,* **9** (2015) 9507.
[60] F. Liu, J. Zhou, S. Wang, B. Wang, C. Shen, L. Wang, Q. Hu & Q. Huang, A. Zhou, "Preparation of high-purity V_2C MXene and electrochemical properties as Li-Ion batteries" Journal of the Electrochemical Society, **164** (2017) A709.
[61] H.J. Monkhorst & J.D. Pack, "Special points for Brillouin-zone integrations", Phys. Rev. B **13** (1976) 5188.
[62] J.P. Perdew, K. Burke & M. Ernzerhof, "Generalized gradient approximation made simple", Phys. Rev. Lett. **77** (1996) 3865.
[63] M. Methfessel & A.T. Paxton, "High-precision sampling for Brillouin-zone integration in metals", Phys. Rev. B **40** (1989) 3616.
[64] P.E. Blochl, O. Jepsen & O.K. Andersen, "Improved tetrahedron method for Brillouin-zone integrations", Phys. Rev. B **49** (1994) 16223.
[65] Y. Wang, M. Zhou, L.C. Xu, W. Zhao, R. Li, Z. Yang, R. Liu & X. Li, Achieving superior high-capacity batteries with the lightest Ti 2 C MXene anode by first-principles calculations: Overarching role of S-functionate (Ti_2CS_2) and multivalent cations carrier. Journal of Power Sources **451** (2020) 227791.
[66] T. Yu, Z. Zhao, L. Liu, S. Zhang, H. Xu & G. Yang, "TiC Monolayer with High Specific Capacity for Sodium-Ion Batteries", J. Am. Chem. Soc. **140** (2018) 5962.