Two-dimensional Nb-based M_4C_3 Solid Solutions (MXenes)

Jian Yang,[a,b,†] Michael Naguib,[c,†,*] Michael Ghidiu,[a] Li-Mei Pan,[b] Jian Gu,[b] Jagjit Nanda,[c] Joseph Halim,[a,d] Yury Gogotsi,[a] and Michel W. Barsoum[a,*]

[a] Department of Materials Science and Engineering and A. J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, Pennsylvania 19104, United States

[b] College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, China

[c] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37381, United States

[d] Thin Film Physics Division, Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-583 31 Linköping, Sweden.

[†] These two authors contributed equally to this work

Herein, two new two-dimensional Nb_4C_3-based solid solutions (MXenes), $(Nb_{0.8},Ti_{0.2})_4C_3T_x$ and $(Nb_{0.8},Zr_{0.2})_4C_3T_x$ (where T is a surface termination) were synthesized – as confirmed by X-ray diffraction - from their corresponding MAX phase precursors $(Nb_{0.8},Ti_{0.2})_4AlC_3$ and $(Nb_{0.8},Zr_{0.2})_4AlC_3$. This is the first report on a Zr-containing MXene. Intercalation of Li ions into these two compositions, and the single-element $Nb_4C_3T_x$ was studied to determine the potential of those materials for energy storage applications. The MXene composition and structure were shown to affect Li intercalation. Lithiation and delithiation peaks at 2.26 V and 2.35 V, respectively, appeared in the case of $Nb_4C_3T_x$, that were not present in Nb_2CT_x. After 20 cycles at a rate of C/4, the specific capacities of $(Nb_{0.8},Ti_{0.2})_4C_3T_x$ and $(Nb_{0.8},Zr_{0.2})_4C_3T_x$ were 158 mAh·g^{-1} and 132 mAh·g^{-1}, respectively - slightly lower than the capacity of $Nb_4C_3T_x$.

I. Introduction

Two-dimensional (2D) materials beyond graphene such as hexagonal boron nitrides, transition metal- dichalcogenides,[1] oxides,[2] and hydroxides,[3] have attracted much renewed attention due to their unique properties. Recently a new family of 2D early transition metal carbides and carbonitrides (so-called MXenes) emerged in the world of 2D materials beyond graphene. MXenes are produced by selective etching of the "A" layers from $M_{n+1}AX_n$ phases.[4] The latter are layered metal carbides and nitrides with a general formula $M_{n+1}AX_n$, (MAX), where M is an early transition metal, A is an A-group element (mostly groups 13 and 14), X is carbon and/or nitrogen, and *n* = 1, 2, or 3. Higher-order MAX phases, with *n* values beyond 3, such as $(Ti_{0.5}Nb_{0.5})_5AlC_4$,[5] Ta_6AlC_5,[6] and Ti_7SnC_6 [7] were reported as secondary phases in lower order MAX phases samples. Also, MAX phases structures with more complex stacking sequences such as $Ti_5Al_2C_3$[8], which consists of intergrown Ti_2AlC and Ti_3AlC_2, were reported. The MAX phase family numbers over 70 members,[9] not including solid solutions on the M site, such as $(V_{0.5},Nb_{0.5})_2AlC$,[10] A site, such as $Ti_3(Al_{0.5},Si_{0.5})C_2$,[11] or the X site such as $Ti_2Al(C_{0.5},N_{0.5})$.[12] MXenes produced form a variety of MAX phases are an emerging family of low-dimensional ceramic materials with outstanding electrical, mechanical and chemical properties that have been attracting much attention.[13] In this paper, not only we introduce two new members of the MAX family, viz.: $(Nb_{0.8},Ti_{0.2})_4AlC_3$ and $(Nb_{0.8},Zr_{0.2})_4AlC_3$, but as importantly convert them to MXenes.

To date, hydrofluoric acid (HF) has been the main etchant used to convert the

MAX phases to MXenes. Using HF, the following MXenes have been produced: $Ti_3C_2T_x$,[4] Ti_2CT_x, $(Ti_{0.5},Nb_{0.5})_2CT_x$, $(V_{0.5},Cr_{0.5})_3C_2T_x$, Ti_3CNT_x, $Ta_4C_3T_x$,[14] V_2CT_x, Nb_2CT_x,[15] and $Nb_4C_3T_x$,[16] where T_x stands for a general surface termination, such as F, O and OH, resulting from the etching process. The presence of O and OH on the surface of MXenes is not surprising since they were reported before on MAX phase surfaces as well in hydrated environments,[17-18] while the presence of F is due to etching in F-containing solutions.

More recently we have shown that it is possible to etch Ti_3AlC_2 with HCl and a fluoride salt, such as LiF.[19] This technique is milder and results in a conductive, clay-like substance with high volumetric capacitances. In general, MXenes can be produced as multilayered flakes[4; 14-16] or as delaminated layers in a colloidal solution, from which MXene paper and films can be obtained.[19-21]

The unique 2D morphologies, good electronic conductivities and rich chemistries render MXenes promising candidates for applications in sensors,[22] electronic devices, catalysts, support for catalysts,[23-25] conductive reinforcement/additives to polymers[26], electrochemical energy storage,[15; 19-20; 27-30] thermoelectrics,[31-32] and other.[33] Among those, the use of MXenes as electrode materials for lithium ion batteries (LIBs) and supercapacitors has been explored more extensively than other applications. When several non-delaminated MXenes, including Ti_2CT_x,[29] $Ti_3C_2T_x$,[34] V_2CT_x and Nb_2CT_x,[15] were tested as anode materials in LIBs, they showed excellent capabilities to handle high cycling rates. For example, V_2CT_x showed a capacity of 280 $mAhg^{-1}$ at a cycling rate of 1 C and 125 $mAhg^{-1}$ at 10 C.

As importantly, we have shown experimentally that various MXene chemistries result in different electrochemical responses, ranging from different voltage profiles to differing specific capacities. For example, Nb_2CT_x has a specific capacity of around 180 mAh g^{-1} at 1 C which is higher than reported for Ti_2CT_x, 110 mAh g^{-1} at the same rate. This is despite the fact that Nb is heavier than Ti.[15] Values exceeding 400 mAh g^{-1} were reported for films of delaminated Ti_3C_2.[20] Such variation in redox activity and capacity utilization can stem from the fact that these 2D materials can exhibit a wide range of electronic and ionic conductivities by simply changing their elemental compositions and/or surface terminations. MXenes can, then, in principal, be designed and modified for specific battery applications.

Since to date the only element that has been selectively etched from the MAX phases is Al, the MXene subset is restricted to Al-containing MAX phases. It also follows that since Al-containing MAX phases with the M elements of Mo, Zr or Hf currently do not exist,[35] no MXenes based on these metals have been reported so far. Moreover, as the above MXenes list shows, the main focus of synthesis has been on the M_2X (n = 1) and M_3X_2 (n = 2) phases. In a recent paper,[16] we reported on synthesis of $Nb_4C_3T_x$, only the second MXene with n = 3 after $Ta_4C_3T_x$[14] and described its structure and morphology. We further showed that in cold-pressed disc form, $Nb_4C_3T_x$ was the most conductive MXene reported to date. The reason for this state of affairs is the presence of two Nb layers embedded in the M_4X_3 structure that are *not* terminated and thus maintain their metal-like conductivity.

The aims of this work are multifold: The first is to report, for the first time, on

two $M_4C_3T_x$, Nb-based solid solution MXenes, viz. $(Nb_{0.8},Ti_{0.2})_4C_3T_x$ and $(Nb_{0.8},Zr_{0.2})_4C_3T_x$, fabricated from their corresponding MAX precursors, $(Nb_{0.8},Ti_{0.2})_4AlC_3$ and $(Nb_{0.8},Zr_{0.2})_4AlC_3$. The second is to demonstrate that until other A-group elements, apart from Al, can be etched, one way to fabricate MXenes with M elements that do not form Al-containing MAX phases, such as Zr, is to start with MAX solid solutions containing those elements such as done here. The third is to compare intercalation of Li ions into three M_4C_3 MXenes: $Nb_4C_3T_x$, $(Nb_{0.8},Ti_{0.2})_4C_3T_x$ and $(Nb_{0.8},Zr_{0.2})_4C_3T_x$, and Nb_2CT_x.

II. Experimental Details

The MAX phase precursors, Nb_4AlC_3, $(Nb_{0.8},Ti_{0.2})_4AlC_3$, and $(Nb_{0.8},Zr_{0.2})_4AlC_3$ were synthesized starting with commercially available powders: Nb (99.5%, ≤ 44μm; Beijing Xinrongyuan Science and Tech. Co., Ltd, China), Al, Ti and Zr (all 99.9%, ≤ 74 μm; General Research Institute for Nonferrous Metals, Beijing, China) and carbon (99%, ≤ 94 μm; Qingdao Tianhe Graphite Co., Ltd, China). The reagents used for etching were: HF, (48-51 wt.%, Acros, Fair Lawn, NJ，USA), hydrochloric acid (HCl), (38 wt.%, Alfa Aesar, Ward Hill, MA, USA) and lithium fluoride, LiF, (99% purity, Alfa Aesar, Ward Hill, MA, USA).

Fully-dense and predominantly single-phase Nb_4AlC_3, $(Nb_{0.8},Ti_{0.2})_4AlC_3$, and $(Nb_{0.8},Zr_{0.2})_4AlC_3$ polycrystalline samples were prepared by hot pressing of commercial powders listed above. The raw materials were mixed in a molar ratio of (Nb+Ti/Zr):Al:C of 4:1.1:2.7 by ball milling for 24 h in a polyethylene jar flushed with argon, Ar, before sealing it. For both the $(Nb_{0.8},Ti_{0.2})_4AlC_3$ and $(Nb_{0.8},Zr_{0.2})_4AlC_3$ samples, the molar ratios of Nb to Ti or Zr were 0.8:0.2.

The mixed powders were placed into a graphite mold that was pre-sprayed with BN, and compacted with a load corresponding to a stress of 3 MPa. The compacted body was then heated at a rate of 20 °C/min up to 1700 °C in a hot–pressing sintering furnace (Shanghai Chen Rong Furnace Co., Ltd., China) and held for 1 h under a load corresponding to a pressure of 30 MPa under flowing Ar, before cooling to room temperature.

The resulting billets were predominantly single phase. MAX phase powders were prepared by crushing the sintered bodies in a QE-100 pulverizer (Yili Tools Co., China) followed by sieving through a 400-mesh sieve. Only the finest fraction was used for MXene synthesis.

The details of $Nb_4C_3T_x$ synthesis were described in our previous work.[16] In brief, Nb_4AlC_3 powder (< 38 μm particle size), was immersed in 50 % aqueous HF for 96 h at ambient temperature, while stirring with a Teflon coated magnetic stir bar, in the ratio of 1 g of Nb_4AlC_3 powder to 10 ml HF solution. This was followed by cycles of washing with distilled water, centrifuge sedimentation (5 mins at 3500 rpm for each cycle), and decanting, until a pH of ~ 5 was reached. At that point, the sediment was mixed in ethanol and allowed to dry by evaporation. The same washing cycle was used for the other two compositions as well.

The synthesis of $(Nb_{0.8},Ti_{0.2})_4C_3T_x$ followed the same procedure as for $Nb_4C_3T_x$, with the only difference being that the etching was carried out at 50 °C instead of room temperature. For the synthesis of $(Nb_{0.8},Zr_{0.2})_4C_3T_x$, a LiF/HCl solution was used as the etchant. Firstly, LiF was added to a 12 M HCl solution, followed by stirring for 0.5 h to completely dissolve the LiF. The $(Nb_{0.8},Zr_{0.2})_4AlC_3$ powder was

then immersed in the solution for 168 h at 50 °C with stirring. Here again, 1 g of $(Nb_{0.8},Zr_{0.2})_4AlC_3$ powder was added to the 10 ml HCl solution containing 0.6 g of LiF. The washing process after etching was the same as the one described above for $Nb_4C_3T_x$ and $(Nb_{0.8},Ti_{0.2})_4C_3T_x$.

A copper K_α radiation source diffractometer (Rigaku Corporation, Tokyo, Japan) was used to obtain X-ray diffraction, XRD, patterns of the powdered samples. Step sizes of 0.02° and 0.04° were used for the MAX and MXene samples, respectively. In both cases the collection time was 0.5 s per step.

The MAX and MXene powders' morphologies were imaged in a scanning electron microscope, SEM (Zeiss Supra 50VP, Oberkochen, Germany) equipped with an energy-dispersive spectrometer, EDS (Oxford Inca X-Sight , Oxfordshire, UK). To calculate global elemental ratios, EDS scans were performed at low magnifications (in the range of 100-200 X) at random points of the powdered samples. Each sample was measured three times and the results averaged. The elemental standards used were: C: $CaCO_3$; Al:Al_2O_3; O:SiO_2; F:MgF_2; Nb:Nb metal; Ti:Ti metal; Zr:Zr metal. XPP matrix correction (Pouchou and Pichoir, 1988) was used for element quantitative analysis. A transmission electron microscope, TEM, (JEOL JEM-2100, Japan) using an accelerating voltage of 200 kV was used in this study. The TEM samples were prepared by dropping several drops of deionized water in which a small amount of the MXene powder was dispersed by sonication for 10 minutes, onto a copper grid and dried in air.

X-ray photoelectron spectroscopy (XPS) was used to determine the chemical

states of the various species in all MAX and MXene samples fabricated herein. The samples measured were in the form of cold press discs. XPS data for Nb_4AlC_3 and $Nb_4C_3T_x$ were taken from [36]. XPS data of $(Nb_{0.8},Ti_{0.2})_4C_3T_x$, and $(Nb_{0.8},Zr_{0.2})_4C_3T_x$ were obtained using a spectrometer (Physical Electronics VersaProbe 5000) employing of a 100 μm monochromatic Al-Kα radiation Photoelectrons were collected by a 180° hemispherical electron energy analyzer. Samples were analyzed at a 45° angle between the sample surface and the path to the analyzer. High-resolution spectra of Nb 3d, Zr 3d, Ti 2p, C 1s, O 1s, and F 1s regions were taken at a pass energy of 23.5 eV, with a step size of 0.05 eV. The spectra were taken after the samples were sputtered with an Ar beam operating at 2.0 kV and 150 μA for 20 minutes. All binding energies were referenced to that of the Fermi level (E_f = 0 eV).

The MXene resistivities were measured on thin discs (200 to 300 μm) that were made by cold pressing MXene powders at 1 GPa in a steel die, 25.4 mm in diameter. The measurements were performed with a 4-point probe (ResTest v1, Jandel Engineering Ltd., Bedfordshire, UK).

The details of the electrochemical measurements were described previously.[15] In short, the MXene powders were mixed with acetylene carbon black (Alfa Aesar, Ward Hill, USA) and 10 wt.% polyvinylidene fluoride (Alfa Aesar, Ward Hill, USA) that was dissolved in 1-methyl-2-pyrrolidinone (Alfa Aesar, Ward Hill, USA) in a 80:10:10 weight ratio. The mixture was then coated onto Cu foil using a doctor blade and dried under vacuum at 140 °C for 12 h, producing a ~ 60 μm thick electrode. CR-2032 stainless steel coin cells (Hohsen Corp. Japan) were assembled using a crimping

machine in an Ar filled glove box. The cells consisted of a MXene electrode and a Li foil (Alfa Aesar, Ward Hill, USA) counter electrode, separated from each other by a sheet of borosilicate glass fiber (Whatman GF/A, Buckinghamshire, UK). The electrolyte was 1.2 M $LiPF_6$ solution in a mixture of ethylene carbonate, EC, and diethyl carbonate, DMC in a 1:2 by weight ratio.

Cyclic voltammetry, CV, tests were carried out on the assembled coin cells using a VMP3 potentiostat for Nb_2CT_x and $Nb_4C_3T_x$ and a VSP300 potentiostat (both from Biologic, Claix, France) for the $(Nb_{0.8},Ti_{0.2})_4C_3T_x$ and $(Nb_{0.8},Zr_{0.2})_4C_3T_x$ samples.

III. Results and Discussion

XRD patterns of Nb_4AlC_3, $(Nb_{0.8},Ti_{0.2})_4AlC_3$ and $(Nb_{0.8},Zr_{0.2})_4AlC_3$ powders, before, and after, etching are shown in Figs. 1a and b, respectively. Since all the major peaks shown in Fig. 1a, can be indexed to Nb_4AlC_3 peaks, we conclude that these powders were predominantly single phase. The *a* and *c*-lattice parameters of these phases were calculated and are listed in Table 1.

Based on the locations of the 002 peaks of the three MAX phases (inset i in Fig. 1a), it is clear that the *c*-lattice parameters of $(Nb_{0.8},Ti_{0.2})_4AlC_3$ and Nb_4AlC_3 phases are comparable; while that of the $(Nb_{0.8},Zr_{0.2})_4AlC_3$ phase is significantly larger. Interestingly, when the 106 peaks are compared (inset ii in Fig. 1a), it is obvious that the Ti- and Zr-containing peak locations fall on either side of those of Nb_4AlC_3. Neither of these observations are surprising given that the atomic radii of Ti (140 pm) and Zr (155 pm) fall on either side of Nb (145 pm).

Table 1 lists the elemental ratios – determined from EDS - in the MAX samples

before, and after, etching. For the $(Nb_{0.8},Ti_{0.2})_4AlC_3$ and $(Nb_{0.8},Zr_{0.2})_4AlC_3$ samples, both the Ti:Nb and Zr:Nb atomic ratios were ≈0.89:4.00; values that are close to the initial nominal compositions. From the totality of the results, it is reasonable to conclude that phase-pure $(Nb_{0.8},Ti_{0.2})_4AlC_3$ and $(Nb_{0.8},Zr_{0.2})_4AlC_3$ solid solution compositions, with Nb/M ratios that are close to their nominal ratios, were obtained.

Like in all our previous work,[33] etching resulted in the following changes to the XRD patterns, chemistries and morphologies of the MAX phases: i) Most of the peaks belonging to the MAX phases either disappeared completely, or were greatly diminished in intensity; ii) the 002 peaks were reduced in intensity, broadened and downshifted considerably (see inset in Fig. 1b). The downshifts correspond to significant increases in the *c*-lattice parameters (see Table 1) and has been attributed to intercalation of water and, possibly, ions between the MXene sheets;[33] iii) the 110 peaks (labeled on the right in Fig. 1b) broaden, but do not disappear. The presence of these peaks confirm that the MXene flakes are not delaminated, but stacked; iv) The overall Al content drops precipitously upon etching (Table 1). For example, the Al:Nb ratio in Nb_4AlC_3 drops from 0.64:4.00 before etching to 0.12:4.00 after etching. Note that the Ti:Nb and Zr:Nb ratios dropped slightly (by about 10 %) after etching (see Table 1). As discussed in more detail below. this could be explained by the preferential dissolution of Zr and Ti relative to Nb during etching; v) The SEM micrographs (Fig. 2) confirm the transformation from MAX to MXene and show the typical morphologies of MXene multilayers.[33]

TEM images of sonicated powders confirm the 2D nature of $(Nb_{0.8},Ti_{0.2})_4C_3T_x$

(Fig. 2c) and $(Nb_{0.8},Zr_{0.2})_4C_3T_x$ (Fig. 2d). The selected area electron diffractions (SAED) of the MXene flakes show that – like all other MXenes, they keep the hexagonal basal plane structure inherited from the parent MAX phases.

XPS measurements were performed to study the chemical species of the various elements in the MAX phases and their MXene counterparts. Comparing the Nb 3d region of $(Nb_{0.8},Ti_{0.2})_4AlC_3$ and its MXene, $(Nb_{0.8},Ti_{0.2})_4C_3T_x$, (Fig. 3a) shows mainly Nb-carbide species. There is also an increase in the binding energy (BE) for the MXene compared to that for the MAX. This shift is due to the removal of Al from the MAX structure and its replacement with various terminations of O, OH and/or F, which in turn increases the Nb oxidation state. This has also been observed for $Ti_3C_2T_x$ vs. Ti_3AlC_2, Ti_2CT_x vs. Ti_2AlC, Nb_2CT_x vs. Nb_2AlC and, $Ti_3(CN)_2T_x$ vs. $Ti_3Al(CN)_2$.[36-37] The Ti 2p region (Fig. 3b) shows mainly Ti-carbide species in $(Nb_{0.8},Ti_{0.2})_4AlC_3$ and its MXene $(Nb_{0.8},Ti_{0.2})_4C_3T_x$ [[36]]. Note the significant reduction in the Ti-peak intensity after etching. This suggests that preferential dissolution of Ti is taking place during the etching of $(Nb_{0.8},Ti_{0.2})_4AlC_3$.

Figure 3c shows the Nb 3d region for $(Nb_{0.8},Zr_{0.2})_4AlC_3$ and $(Nb_{0.8},Zr_{0.2})_4C_3T_x$. Here again, the Nb BE increases upon etching. Interestingly, and in contrast to Nb-Ti case (Fig. 3a) in this case, peaks associated with Nb_2O_5 were also detected (Fig. 3c) The Zr 3d region for the $(Nb_{0.8},Zr_{0.2})_4AlC_3$ sample (Fig. 3d), shows mainly the presence of one species belonging to the Zr-carbide [38]. The same region for $(Nb_{0.8},Zr_{0.2})_4C_3T_x$ shows evidence for two species. The first has weak and significantly broad peaks that belong to Zr-bonded to C. The second, has relatively

stronger peaks that belongs to ZrO_2 [36]. Based on these results it is reasonable to conclude that upon etching the Zr atoms are selectively etched, and subsequently oxidized, from the parent MAX phase. More details about the XPS results can be found in the supporting information.

The C peaks of M-carbide species in the MAX and MXene, for all three systems, all have identical binding energies. This implies that while etching clearly modifies the M-atoms, it does not modify the chemical state of the C in these structures (Figs. S1b, S2a and b).

XPS measurements of O1s region for $Nb_4C_3T_x$ (Fig S3a) evidence the presence of –O, -OH and –OH-H_2O_{ads}, terminations where the latter is adsorbed water on the –OH terminations, these species were identified and studied in [36]. Similarly XPS measurements of F 1s region for $Nb_4C_3T_x$ (Fig S3b) shows the presence of –F terminations.

Quantifying or even identifying the nature of the termination species in the O 1s, and F 1s regions for the solid solutions $(Nb_{0.8},Ti_{0.2})_4C_3T_x$ and $(Nb_{0.8},Zr_{0.2})_4C_3T_x$ is significantly more complicated – because of the presence of two different M elements. More in-depth studies are required that are beyond the scope of this paper.

Small peaks belonging to $(Nb_{0.8},Zr_{0.2})_4AlC_3$ were recorded in the XRD pattern of that powder after etching (Fig. 1b, top), implying that the etching was incomplete in this case. There is little doubt however, that the majority of this powder was etched. For example, the Al:(Nb+Zr) ratio dropped from 0.95:4.00 before etching to 0.16:4.00

after. The etching slightly altered the Zr:Nb atomic ratio, to 0.82:4.00, which is consistent with the selective etching of Zr. The etching products of $(Nb_{0.8},Ti_{0.2})_4AlC_3$ and $(Nb_{0.8},Zr_{0.2})_4AlC_3$ still show a shift of the XRD peaks toward higher and lower angles, respectively, as compared to $Nb_4C_3T_x$ (see inset in Fig. 1b). A more careful examination of the increases in *c*-lattice parameters of the three MXenes listed in Table 1, indicate that while the increases for the Nb_4AlT_x and $(Nb_{0.8},Ti_{0.2})_4AlT_x$ MXenes - relative to their MAX phase precursors - were ≈ 25 %. In contrast, the increase in the case of the Zr-containing MXene, was closer to ≈ 42%. It follows that, for reasons that are not clear, there are more water layers between the flakes of the latter than the former. What exactly determines the post-etching *c*-lattice parameters is still unclear and remains a topic of intense research at this time. This comment notwithstanding, given the starting reagents, the choice of what is between the layers has to be water and/or solvated ions. The resistivities of the Nb-, Nb-Zr-, and Nb-Ti-based compositions were measured to be 3100, 5700 and 3400 μΩm, respectively. In previous work we reported resistivity values of 4600 μΩm and 2×10^5 μΩm, for discs of $Nb_4C_3T_x$ and Nb_2CT_x cold pressed to 1 GPa.[19] The differences in the resistivities between the $Nb_4C_3T_x$ samples measured herein and previous work may be due to different contents of water, incomplete etching among other factors.

The CVs of Nb_2CT_x (Figs. 4 a and b) show two reversible lithiation peaks (I) and (II) at voltages around 1.45 V and close to 0 V, respectively. The corresponding delithiation peaks (I'), and (II') are found around 1.56 V and 0.65 V, respectively. The intensity of peak (II'), however, decreased significantly after 20 cycles (dashed grey

curve in Fig. 4 a and b).

For $Nb_4C_3T_x$, (Figs. 4 c and d) an extra lithiation peak around 2.26 V with a corresponding delithiation peak around 2.35 V is observed. The delithiation peak around 0.6 V vanishes and a new peak (III') around 0.3 V appeared after 3 cycles.

When the areas of the CVs for Nb_2CT_x and $Nb_4C_3T_x$, shown in Figs. 4 a and c, are compared, it is clear that, on an absolute scale, the Li capacity of the former is higher than the latter. For example, after 25 cycles, the Li capacities of the Nb_2CT_x and $Nb_4C_3T_x$ compositions were 222 and 189 $mAh \cdot g^{-1}$, respectively. This is a somewhat surprising result because, all else being equal, the gravimetric capacity of $Nb_4C_3T_x$ should be roughly 50 % lower than that of its lighter Nb_2CT_x counterpart. Based on those capacities then the lithiated chemistries are $Li_{1.9}Nb_2C_{0.9}O_{1.2}(OH)_{0.6}F_{0.3}$ and $Li_{3.1}Nb_4C_{2.3}O_{0.7}(OH)_{0.8}F_{0.7}$ (the nominal compositions of the MXenes before lithiation were found using XPS and the Li content was estimated from the capacity using Faraday's law). [36-37] The more Li atoms stored in case of $Nb_4C_3T_x$ can be correlated to the new peaks appearing in the CVs and could possibly be assigned to the formation of a 2nd Li layer predicted in Ref. [39].

Since it is reasonable to assume that both Nb_2CT_x and $Nb_4C_3T_x$ would have similar surface species, the existence of new peaks and the higher number of Li atoms stored in case $Nb_4C_3T_x$ compared to Nb_2CT_x can only be explained by differences in their electronic structures leading to the formation of a 2nd Li layer. Using DFT calculations, Xie and Kent [40] found that increasing the *n* value in $Ti_{n+1}X_nT_x$ results in different electronic structures. For example, the density of states, DOS, at the Fermi

level, for Ti_2CO_2, $Ti_3C_2O_2$ and $Ti_4C_3O_2$ were predicted to be ≈ 0, 0.58 and 0.98, respectively.[40] The fact that $Nb_4C_3T_x$ is roughly two orders of magnitude more conductive than Nb_2CT_x [16] may contribute to higher Li-ion uptake per layer. These comments notwithstanding it is hereby acknowledged that more work is needed to better understand these important differences.

Substituting 20 at. % of the Nb atoms by Ti or Zr atoms did not result in significant changes in electrochemical performance compared to $Nb_4C_3T_x$. This is best shown in Figs. 5a and b, where only slight differences in the CV recorded were observed of $Nb_4C_3T_x$ compared to its Ti, and Zr solid solutions counterparts. The main difference between $Nb_4C_3T_x$ and its solid solutions after five cycles (Fig. 5 b) is the higher capacity of the former at low voltages (below 1.00 V). Also, in case of Nb-Ti solid solution, a stronger delithiation peak at 1.64 V exists. During the first cycle (Fig. 5a), in case of the Ti-Nb MXene a new lithiation peak appeared at 1.43 V compared to the peak at 1.10 V for $Nb_4C_3T_x$. The delithiation peak around 2.35 V in case of $Nb_4C_3T_x$ and its Ti solid solution does not exist in case of the Nb-Zr solid solution MXene.

The first discharge cycle shows higher capacity due extra lithium consumed to form the reductive passivation layer normally called as the SEI (Solid-Electrolyte Interface) layer. The specific capacities, estimated from the CVs after 20 cycles, are plotted in Fig. 6. After 20 cycles, the specific capacities for $Nb_4C_3T_x$, $(Nb_{0.8},Ti_{0.2})_4C_3T_x$, $(Nb_{0.8},Zr_{0.2})_4C_3T_x$ were 189 $mAh \cdot g^{-1}$, 158 $mAh \cdot g^{-1}$, and 132 $mAh \cdot g^{-1}$, respectively. In all the cases the coulombic efficiency was more than 99 %

after 20 cycles. It is worth noting that all the specific capacities reported here are lower than commercial graphite, which has a capacity of ~ 372 $mAh \cdot g^{-1}$.

IV. Summary and Conclusions

For the first time, two Nb_4AlC_3-based solid solution MAX phases $(Nb_{0.8},Ti_{0.2})_4AlC_3$ and $(Nb_{0.8},Zr_{0.2})_4AlC_3$, and their corresponding MXenes, $(Nb_{0.8},Ti_{0.2})_4C_3T_x$ and $(Nb_{0.8},Zr_{0.2})_4C_3T_x$, were synthesized. The latter is the first Zr-containing MXene reported to date.

Theoretically, the specific capacity of $Nb_4C_3T_x$ should be about 50% less than its 211 counterpart, Nb_2CT_x. Our results, however, show that after 25 cycles, $Nb_4C_3T_x$ still retained a specific capacity(189 $mAh \cdot g^{-1}$) that was ~ 85 % of that of Nb_2CT_x (222 In addition, a new lithiation peak around 2.26 V and a corresponding delithiation peak around 2.35 V appeared. This result is attributed to the intercalation of a larger number of Li atoms per layer in $Nb_4C_3T_x$, compared to Nb_2CT_x.

Substituting 20 at. % of Nb atoms by Ti or Zr atoms did not result in significant changes in Li uptake compared with $Nb_4C_3T_x$. $(Nb_{0.8},Ti_{0.2})_4C_3T_x$ and $(Nb_{0.8},Zr_{0.2})_4C_3T_x$ showed a specific capacity of 158 $mAh \cdot g^{-1}$ and 132 $mAh \cdot g^{-1}$ after 20 cycles, respectively.

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Figures Captions:

Fig. 1: XRD patterns of the three MAX samples, a) before and, b) after etching. Insets in (a) and (b) show partially enlarged XRD patterns. The peaks marked by green squares represent NbC present as a phase impurity; those marked by red circles represent unreacted MAX phase in the MXene sample.

Fig. 2: Typical post-etching SEM images of; a) $(Nb_{0.8},Ti_{0.2})_4C_3T_x$ and, b) $(Nb_{0.8},Zr_{0.2})_4C_3T_x$ powders, and TEM images of a) $(Nb_{0.8},Ti_{0.2})_4C_3T_x$ and, b) $(Nb_{0.8},Zr_{0.2})_4C_3T_x$ nanosheets. The insets in c) and d) are the corresponding SAED of the $(Nb_{0.8},Ti_{0.2})_4C_3T_x$ and $(Nb_{0.8},Zr_{0.2})_4C_3T_x$ MXenes flakes, respectively.

Fig. 3 XPS spectra for (a) Nb 3d and, (b) Ti 2p regions in the MAX phase $(Nb_{0.8},Ti_{0.2})_4AlC_3$ (bottom black) and its MXene, $(Nb_{0.8},Ti_{0.2})_4C_3T_x$ (top red) and, (c) Nb 3d and, (d) Zr 3d regions in the MAX phase $(Nb_{0.8},Zr_{0.2})_4AlC_3$ (bottom black) and its MXene,$(Nb_{0.8},Zr_{0.2})_4C_3T_x$ (top, red).

Fig. 4: Cyclic voltammograms obtained at a rate 0.2 $mV{\cdot}s^{-1}$ for, (a) Nb_2CT_x and, (c) $Nb_4C_3T_x$. (b) and (d) are the same as (a) and (c) respectively, but with smaller Y-axes ranges.

Fig. 5: Cyclic voltammograms obtained at a rate of 0.2 mV/s for $Nb_4C_3T_x$ (red lines with circles), $(Nb_{0.8}Ti_{0.2})_4C_3T_x$ (blue lines with squares), and $(Nb_{0.8}Zr_{0.2})_4C_3T_x$ (green lines with triangles), (a) 1^{st} cycle (d) 5^{th} cycle.

Fig. 6: Specific capacities on charging (squares) and discharging (circles) of $Nb_4C_3T_x$ (red lines and symbols), $(Nb_{0.8}Ti_{0.2})_4C_3T_x$ (blue lines and symbols), and $(Nb_{0.8}Zr_{0.2})_4C_3T_x$ (green lines and symbols).

Tables:

Table 1: Lattice parameters and elemental ratios, as determined from EDS analysis of the samples before and after etching. In all cases, the Al concentrations dropped and the *c*-lattice parameters increased significantly after etching. M refers to Ti or Zr. Numbers in brackets show standard deviation.

Material	M:Nb	Al:(Nb+M)	*a* (nm)	*c* (nm)
Nb_4AlC_3		0.64 (0.08):4.00	0.313	2.422
$Nb_4C_3T_x$		0.12 (0.02):4.00	0.315	3.059
$(Nb_{0.8},Ti_{0.2})_4AlC_3$	0.89 (0.02):4.00	0.84 (0.02):4.00	0.312	2.417
$(Nb_{0.8},Ti_{0.2})_4C_3T_x$	0.84 (0.02):4.00	0.10 (0.01):4.00	0.313	2.969
$(Nb_{0.8},Zr_{0.2})_4AlC_3$	0.89 (0.02):4.00	0.95 (0.03):4.00	0.316	2.441
$(Nb_{0.8},Zr_{0.2})_4C_3T_x$	0.82 (0.02):4.00	0.16 (0.02):4.00	0.316	3.477