Two Dimensional $Ti_3C_2T_x$ MXene Electrode For Supercapacitor Application

Fatma Nur Tuzluca
Department of Physics, Faculty of Art and Science, Erzincan Binali Yıldırım University, Erzincan, Turkey

Yasar Ozkan Yesilbag
Department of Physics, Faculty of Art and Science, Erzincan Binali Yıldırım University, Erzincan, Turkey

Farah Nabilah Shafiee
Institute of Advanced Technology, Universiti Putra Malaysia, Selangor, Malaysia

Mohd Nizar Hamidon
Institute of Advanced Technology, Universiti Putra Malaysia, Selangor, Malaysia

Mehmet Ertugrul
Department of Electrical and Electronics Engineering, Faculty of Engineering, Atatürk University, Erzurum, Turkey
ertugrul@atauni.edu.tr

Abstract— **Two-dimensional materials are one of the most studied materials for many applications in recent years. Among the two-dimensional (2D) metal carbide, MXene is seen as one of the most promising materials for energy storage systems. Among the MXene family, $Ti_3C_2T_x$, the lightest material, is one of the electrode materials due to its unique electrochemical performance. In this study, $Ti_3C_2T_x$ MXene structure was obtained by removing Al layer from Ti_3AlC_2 MAX structure by selective etching. Exceptional electrochemical performance and high electronic conductivity of $Ti_3C_2T_x$ was obtained and surface and morphological analyzes were performed with FESEM, EDS, XRD. FESEM has demonstrated that synthesized MXene is a layered solid structure. In addition, synthesized MXene was tested for electrochemical behavior against electrochemical energy storage applications using techniques such as cyclic voltammetry (CV), galvanostatic charge discharge (GCD), and electrochemical impedance spectroscopy (EIS). Characterization and electrochemical tests have shown promising performance in electrochemical charge storage applications.**

I. INTRODUCTION

The MXene, known as transition metal carbides, carbonitrides and nitrides are the most recently added structures in the 2D family of materials and are promising due to their versatile surface chemistry [1]. MXenes are obtained by selective etching the 'A' atomic layers from the layered structures of the MAX phases, and are named as MXene due to their 'MX' layered structures emphasizing the similarity to the graphene so as the 'ene' suffix. Although the compatibility of MXenes to electromagnetic radiation absorption [2], composites strengthening [3], water treatment [4], gas sensors [5], biosensors [6], cancer treatment [7], lubricants [3], field effect transistors [8], transparent conductors [9], photochemical and electrochemical catalysis [10] applications via theoretical and experimental studies due to their adjustable electronic, optical, plasmonic [11] and thermoelectric [12] properties, the most studied field of application is energy storage [13]. MXenes have high electrical conductivity, superior electron-transfer capability, charge-carrying mobility, large surface area, good mechanical properties and transparency. MXene-based supercapacitors are of great interest among electrochemical energy storage devices due to their high-power density, high charge-discharge efficiency and long cycle life. In the literature, more than 70 structures related to MAX phases have been studied [14]. So far, 21 MXene structures are obtained experimentally from those MAX phases [15]. While the M-X bond of MAX layered structure has covalent/metallic/ionic character, the M-A bond has metallic character. However, since the M-A bond between the layers and the A-A bond between the atoms are rather weak compared to the M-X bond, the higher chemical reactivity of the "A" atomic layer, i.e., its corrosivity with aqueous acid solutions (HF or LiF+HCl) is facilitated. In other words, the main reason for obtained MXene from MAX phases by chemical etching is that the M-A bond is much weaker than the M-X bond [14]. Selective etching is the most important condition for obtaining MXene from MAX phases. Today, the most common method for synthesizing MXene is wet etching [13]. The most important parameters in this method are acid concentration, reaction time and temperature. Especially in the studies related to MXene synthesis, easy controllability and efficiency of reaction parameters are the reason of choice of this method. Thus, acidic solutions containing predominantly aqueous fluoride are used to selectively etching the "A" element layers from the MAX layered structures. So, to obtain MXene, H^+ and F^- ions must be present in the solution. MXene layers which are in good contact with the coplanar planes after etching are subjected to intercalation process. The intercalation process results in delamination, which occurs by ultrasonication of MXene layers in water with different polar organic molecules or large organic-based molecules. Thus, the intercalating species / molecules allow delamination to increase the distance between the layers. Few mechanical vibrations also accelerate delamination. MXenes that are synthesized using solutions with acidic-fluoride have structure terminations with OH, O, and F as seen in the chemical formula $M_{n+1}X_n(OH)_xO_yF_z$. Briefly, this chemical formula has the general expression $M_{n+1}X_nT_x$ (n=1-3), where M represents a transition metal (Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, Mn), X is carbon (C) and nitrogen (N), T_x represents hydroxyl (OH), oxygen (O) and fluorine (F) [1]. For example, $Ti_3C_2T_x$ is the most studied MXene in supercapacitor applications. While

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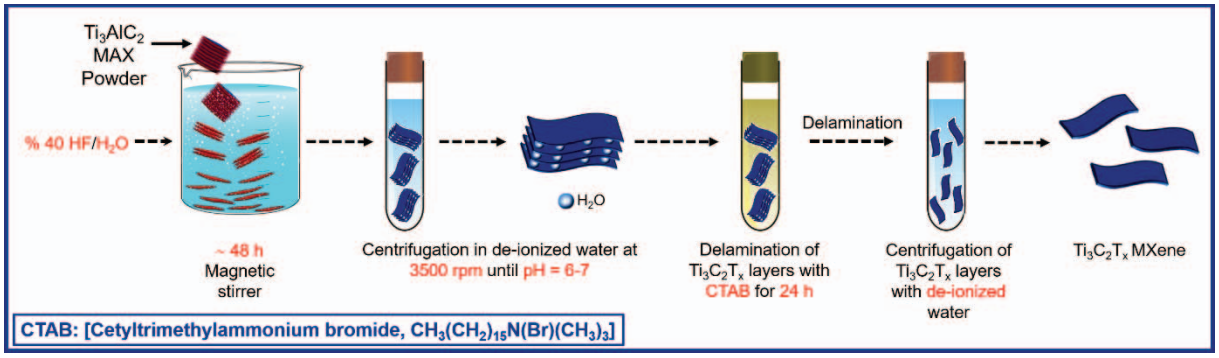


Fig. 1. Synthesis of $Ti_3C_2T_x$ MXene structure from Ti_3AlC_2 MAX phase.

the volumetric capacitance of $Ti_3C_2T_x$ electrode in neutral and aqueous electrolytes is 300–400 F cm^{-3}, the volumetric capacitance value in 1 M H_2SO_4 exceeds 900 F cm^{-3}. These capacitance values are due to the fact that the protons, the smallest cations, reach a greater number of electrochemically active sites and prevent their ions from aggregating into the MXene layers during intercalation. In addition, these values are greater than the value of graphene (350 F cm^{-3}), a carbon-based electrical double-layer capacitor (EDLC).

Also, the $Ti_3C_2T_x$ MXene shows excellent pseudocapacitive behavior even at very high charge and discharge rates. Thin $Ti_3C_2T_x$ MXene electrodes imprinted on flexible substrates perform better at higher charge-discharge rates. Furthermore, these $Ti_3C_2T_x$ MXene have excellent cycle stability without any decrease in capacitance even after 10000 charge-discharge cycles.

II. Materials and Methods

In this study, the $Ti_3C_2T_x$ MXene structure was obtained by etching the Al layers from the synthesized Ti_3AlC_2 MAX phase as expressed in Figure 1. 2 g of Ti_3AlC_2 layered powder was mixed in 20 ml 40% HF: H_2O solution at 25°C for 48 h. The resulting $Ti_3C_2T_x$ MXene layers were repeated centrifuged by adding de-ionized water at 3500 rpm until the pH value was ~6-7. This MXene was then rinsed with CTAB in a magnetic stirrer for 24 h and centrifuged with de-ionized water to increase the distances between the layers. Water was removed from the structure by an additional drying process (80-100°C in the oven).

III. Results and Discussion

The structure, morphology and elemental analysis of the $Ti_3C_2T_x$ MXene was carried out using the X-ray diffractometer technique (PANalytical Empyrean, Cu-Kα, λ=1.54060 Å), a field-emission scanning electron microscope (FESEM: FEI Quanta 450 FEG) and an EDS analyzer in the FESEM system (EDAX, AMETEK Materials Analysis Division) respectively. Cyclic voltammetry (CV), galvanostatic charge discharge (GCD) and electrochemical impedance spectroscopy (EIS) analysis of the $Ti_3C_2T_x$ MXene was performed via Gamry Interface 1010E potentiostat. The FESEM images and EDS analyzes of the synthesized $Ti_3C_2T_x$ MXene structure is given in Figure 2.

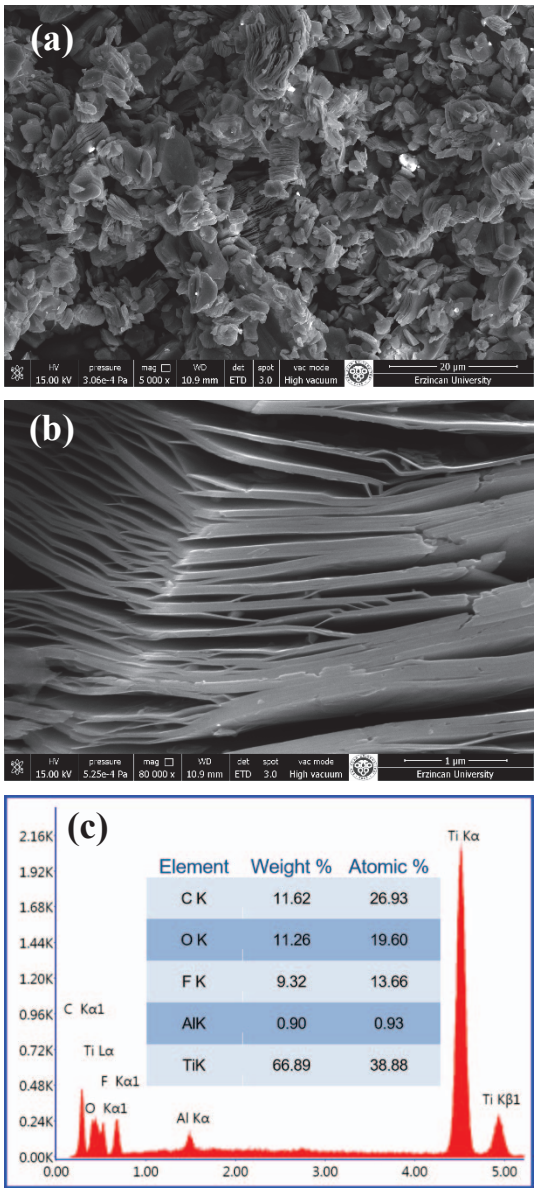


Fig. 2. (a) Low and (b) high magnification FESEM images and (c) EDS results of the $Ti_3C_2T_x$ MXene.

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IV. Conclusion

In summary, $Ti_3C_2T_x$ MXene was synthesized by the successful etching of Al from Ti_3AlC_2. The effect of the mass ratios of Ti_3AlC_2 to HF on the electrochemical performance of electrodes for supercapacitors was investigated. Excellent electrochemical performance has shown that layered $Ti_3C_2T_x$ is a promising electrode material for high power and high energy devices.

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