MXene-Based Electrolyte for Vanadium-Bromide Redox Flow Battery for Green Energy

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Abstract

New promising technology has been developed in 1984 for vanadium redox flow batteries into stagnant energy storage. Compared to other redox flow battery systems, this technology is very efficient, low cost, and has longer life. However, vanadium redox flow batteries need to overcome low thermal conductivity, low diffusivity, high resistivity, high liquid density, and low energy efficiency. This study aims to use MXene in vanadium (IV) electrolytes to improve thermal conductivity and diffusivity and reduce resistivity. The vanadium (IV) electrolyte-based nanofluid was studied with a different weight percentage of MXene (0.5wt%, 1wt%, 1.5wt%, and 2.0wt%). Several physical, thermal and electrochemical characterizations like FTIR, UV-Vis, SEM, EDX, and thermal properties measurements were performed. The FTIR, UV-Vis and SEM, and EDX show there is no additional peak observed, the reduced light transmission capability was enhanced and smooth 2D layered structures of MXene were obtained. MXene-based electrolyte's highest value of thermal conductivity was increased against base solution by 29.8%, 53.6%, 70.3%, and 75.9%, and the resistivity decreased by 30.7%, 47.4%, 65.2%, and 68.9%, respectively. The best thermal conductivity increased by 75.9% using 2wt% MXene at 45°C. Due to the enhancement of physical, thermal, and electrochemical characterizations, this study will help guide future research to improve green energy storage technology and reach some of the sustainable development goals (SDG) to ensure the access to affordable, reliable, sustainable and green modern energy for all.

Keywords: MXene, redox flow battery, nanofluid, green energy, energy storage.

1.0 Introduction

Traditional power generation emits a lot of CO_2 but is the most significant aspect for all countries. Renewable green energy sources including solar, wind, and biogas minimize CO_2 emissions. A large-scale energy storage problem has emerged following the completion of power generation [1]. High efficiency, low cost, and long-life cycle make redox flow batteries excellent for large-scale energy storage. Each redox couple's electrochemical potential is unique; they can provide an electromotive force that drives oxidation-reduction processes. Vanadium redox flow batteries (VRFBs) are proposed for ESS [2]. Vanadium sulphate solution is used to make both positive (VO^{2+}/VO_2^+) and negative (V^{2+}/V^{3+}) electrolytes. With its low energy density (less than 25 Wh kg^{-1}), the VRFB is no longer commonly employed in the automotive industry. It is reliable, flexible, and extended cycle life for enhancing the energy density of stationary storage [3]. Vanadium Bromide Redox Flow Battery (V-Br RFB) is a large-scale energy storage system with high energy density [4]. The V^{2+}/V^{3+} pair is placed in the negative half-cell with vanadium halide and the couple in the positive half-cell. Vanadium bromide, hydrobromic acid, and hydrochloric acid are half-cell electrolytes. ' Vanadium halides (3–4 M) are highly soluble than vanadium sulphate salts in the V/Br battery. This allows for an almost twofold increase in energy density (theoretically 50 Wh kg^{-1}) [4,5].

The $Br/ClBr_2$ or $Cl/BrCl_2$ redox couple is used in the positive half-cell of the V/Br, whereas the V^{2+}/V^{3+} redox couple is used in the negative half-cell. Because of the high concentration of halide ions in the V/Br cell electrolyte, it is possible to reduce the capacity of the positive half-cell reservoir virtually in half during charging [5,6]. This is achievable because the V/Br cell electrolyte contains a substantial amount of halide ions. As a result, the total volume of electrolytes may be reduced by up to 25%, further increasing the V/Br cell's energy density. In comparison to vanadium redox flow batteries, the V-Br RFBs exhibited the advantages of high solubility and energy density, and there was no risk of cross-contamination. Because the V-Br RFBs employed the same elements in both the positive and negative electrolytes, these benefits were attainable. The V^{2+}/V^{3+} redox couple reaction and the Br/Br_3 reactions are used by the V-Br electrolyte to charge and discharge negative and positive half-cells, respectively shown in fig 1(a) [6]. Redox flow batteries can benefit from MXene's high conductivity, hydrophilicity, large surface area, and stability at anodic potentials. Chemical compositions, interlayer spacing,

intercalation, and hybridization are accessible [7]. MXenes have the potential to be electrode materials in redox flow batteries [8]. In the Ti_3C_2 layer structure, redox reactions may be carried out on exposed and unsaturated Ti-atoms. Using layered Ti_3C_2 reduces the battery's ohmic resistance, which has metallic characteristics and great electrical conductivity [9]. Due to its stability and catalytic activity, it has high energy efficiency and current density in redox flow batteries[10]. In this work, a simple electrolyte's preparation method of V-Br RFB is presented. The VBr_3 solution was electrolyzed to produce V^{2+}/V^{3+}. $Ti_3C_2T_x$ are mixing to prepared for measuring the thermal conductivity, diffusivity, and resistivity, stability at 30°C-45°C. After mixing $Ti_3C_2T_x$ can increase the active surface area and accelerate electron transfer and heat exchange properties of V-Br RFB. The thermophysical performance of the V-Br RFB is outstanding with different wt% of $Ti_3C_2T_x$ -based VBr3 electrolytes. Thermal conductivity increased and resistance dropped respectively.

2.0 Materials and Methods

2.1 Preparation of the Electrolyte

Vanadium Bromide (VBr_3), and H_2SO_4 were acquired from (Alfa Aesar 99.5% and Fisher Scientific, respectively. Dissolving 1M VBr_3 in 2.5M H_2SO_4 and stirring at 1200 rpm for 3 hours with a magnetic stirrer produced the positive electrolyte. The VBr_3 solution was electrolyzed to produce the negative electrolyte (V^{3+}), and titration with 0.1 M potassium permanganate revealed that it did indeed contain. Hydrochloric acid (HCl) (Fisher Scientific, 37%) was added to the electrolytes at a concentration of 5M respectively and mixed again for 3 hours at 1200 rpm, and the temperature was maintained at 40°C. Applying the wet-chemistry etching method with NH_4HF_2 as an etching agent produced $Ti_3C_2T_x$[11]. Then the Mxene was included in the electrolyte at weight percentages of 0.5, 1.0, 1.50, and 2.0 wt%. When $Ti_3C_2T_x$ was added, the solution was ultrasonicated for 6 hours at 50% amplitude and stored in the fridge for 48 hours to improve the chemical composition at 5°C.

2.2 Characterization of the Electrolyte

TEMPOS dual needle KS-3 assessed thermal conductivity. Thermal conductivity, diffusivity, and resistivity of MXene-based electrolytes at 25°C-50°C are measured. SEM was used to study the morphology of MXene (JSM-7500F, JEOL). X-ray Energy Dispersive Spectroscopy was used to evaluate MXene's heteroatom distribution (EDS, Oxford Instruments, UK). A vanadium-based electrolyte solution containing MXene was analyzed by FTIR (Model: FTIR Spectrum Two, PerkinElmer). In transmittance mode, 3500–500 cm^{-1} spectra were observed. Ultraviolet-visible spectroscopy assessed optical absorption (UV–Vis, Model: Lambda 750, PerkinElmer, USA) at room temperature, and 800 to 200 nm transmittance data is acquired.

3.0 Results and Discussion

3.1 Thermophysical Measurement

MXene-based V-Br_3 electrolytes with 0.5, 1.0, 1.5, and 2.0 wt% of $Ti_3C_2T_x$ are prepared for measuring the thermal conductivity, diffusivity, and resistivity at 30°C-45°C. Thermal conductivity is the ability of the material to conduct heat. Thermal diffusivity assesses a material's ability to conduct. Thermal resistivity is a heat property and a temperature difference measurement by which an object or material resists a heat flow. The base electrolytes solution of VBr_3's lowest thermal conductivity and diffusivity and resistivity have been found at 0.864, 0.881,0.908, 0.922 Wm^{-1}K^{-1}, 1.297, 1.359, 1.437, 1.538 m^{2}s^{-1}, and 1.231, 1.221, 1.208, 1.198 °K-mW^{-1} at different temperature respectively. By increasing the temperature and wt% of MXene, Table 1 shows that the thermal conductivity and diffusivity are increasing and resistivity is decreasing. After adding different wt% of $Ti_3C_2T_x$ at 45°C, the highest thermal conductivity and diffusivity have been found at 1.168, 1.406, 1.473, 1.681 Wm^{-1}K^{-1}, and 1.81, 2.19, 2.40, 2.65 m^{2}s^{-1}, and the lowest resistivity 0.837, 0.686, 0.641, 0.484 °K-mW^{-1} respectively. The thermal conductivity increased by 29.8%, 53.6%, 70.3%, 75.9%, and the resistivity reduced by 30.7%, 47.4%, 65.1%, and 68.9% at 45°C and 2.0wt% of MXene based electrolytes got the highest improved result. On the other hand, at 0.50 wt% MXene, and at 30°C find the lowest improved result. It is clearly seen in table 1 that by increasing wt% of MXene and temperature, the thermal conductivity and diffusivity are increasing, and resistivity is decreasing. MXene Ti_3C_2 have inherently good conductivity and excellent volumetric capacitance because they are molecular sheets made from the carbides of transition metals like titanium. During the preparation of electrolytes when increased the percent of weight of Ti3C2 (0.5wt%, 1wt%, 1.5wt%, and 2.0wt%) with the increase of temperatures (30-45°C), it had been developed a mechanically robust mass ion transport, conductive coating that can maintain performance under heavy stretching, bending, tunable bandgap, increasing the heat capacity, large elastic moduli, hydrophilic surface, which was increasing the level of thermal conductivity and less resistivity of electrolyte's solutions respectively. In fig 1(d,e). Shows the all-electrolyte solution's thermal conductivity and resistivity changes against the pure VBr_3-based electrolytes.

Table 1MXene-based VBr$_3$ electrolyte's thermal conductivity, diffusivity, and resistivity at different temperatures.

Temperature (°C)	Mxene (wt%)	Thermal Conductivity (W.m^{-1}K^{-1})	Thermal Diffusivity (m^2 s^{-1})	Thermal Resistivity (°K-m/W)	Temperature (°C)	Mxene (wt%)	Thermal Conductivity (W.m^{-1}K^{-1})	Thermal Diffusivity (m^2 s^{-1})	Thermal Resistivity (°K-m/W)
30	0.50	1.129	1.72	0.871	30	1.0	1.275	1.95	0.785
35		1.131	1.75	0.869	35		1.309	2.02	0.757
40		1.159	1.79	0.849	40		1.351	2.10	0.716
45		1.168	1.81	0.837	45		1.406	2.19	0.686
30	1.50	1.363	2.04	0.691	30	2.0	1.576	2.30	0.597
35		1.401	2.11	0.678	35		1.606	2.36	0.574
40		1.456	2.20	0.653	40		1.632	2.47	0.499
45		1.473	2.40	0.641	45		1.681	2.65	0.484

3.2 SEM & EDX

Ti$_3$C$_2$T$_x$ MXene SEM picture. Silky-smooth Ti$_3$C$_2$T$_x$ powder generated multilayered Ti$_3$C$_2$T$_x$MXene. EDX analysis examined the functional groups on Ti$_3$C$_2$T$_x$ MXene nanosheets. Fig. 1(b) shows Ti$_3$C$_2$T$_x$ MXene, and Fig. 1(c) shows its SEM image of the EDX spectrum. C, Ti, O, Cl and F have four significant EDX peaks, whereas Al has just one very small pick. Fig. 1(c) exhibits Ti$_3$C$_2$T$_x$ EDX data. According to the study, Ti$_3$C$_2$T$_x$MXene has 11.67% wt C, 70.46% wtTi, 11.57% wt O, 2.82% wt Cl and 3.32% wt F. Due to F and O, F and OH and COOH are related.
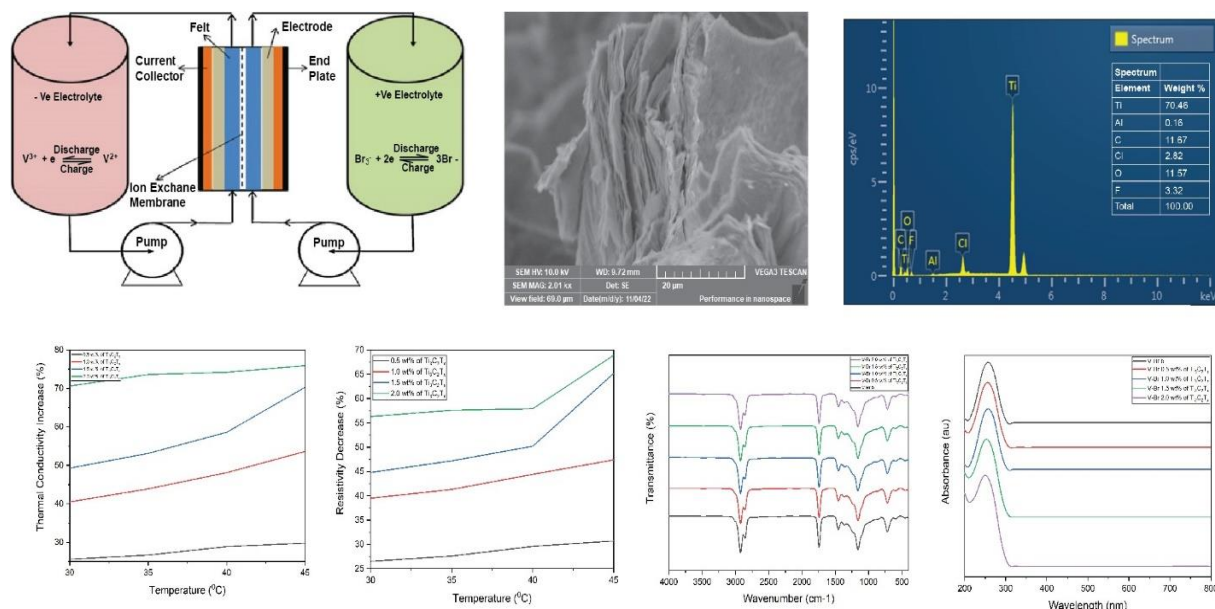

Fig.1. Schematic diagram of V-Br RFB (a), SEM image of Ti$_3$C$_2$T$_x$MXene (b), detected four EDX peaks (c), percent of increased thermal conductivity (d) and decreased resistivity (e), FTIR spectra (f), UV-vis spectra (g) of different %wt of Mxene-based VBr3 electrolytes at room temperature.

3.3 FTIR & UV-vis

FTIR was used to analyze functional groups of untreated and treated samples in fig.1(f) where large absorption peaks at 2928.35 cm^{-1} and 2863.42 cm^{-1} indicate a stretching vibrational mode for -OH groups, as compared to the untreated sample (C=C-OH), which has an additional vibrational band at 1747.67 cm^{-1}. Carbon fibers treated with mixed acids have -OH groups, as seen in these bands. The C=O group of aldehyde, ketone, or lactone can be identified at 1367.14 cm^{-1} and 713.86 cm^{-1}[12]. In all FTIR spectrums, there are no notable changes between the tested samples, hence no chemical contact alters the chemical nature of a substance there. So, from there, it can be considered as chemically stable.

Fig. 1 (g) shows VBr$_3$-based electrolyte solutions with and without MXene. The blank solution has a large absorption peak at 257.3.6 nm. 0.50 wt% MXene does not create a new absorption peak or affect -max. UV–vis spectroscopy is unaffected by 2.0 wt% MXene. This means that extra MXene does not react with vanadium ions. Adding Mxene to the positive electrolyte does not affect the redox process. Fig. 1 (g) displays VBr$_3$ electrolyte solution with and without MXene's UV-vis spectrums. Blank VBr$_3$-based electrolyte solution -max is 251.69 nm

and. After the addition of 0.50 wt%, 1.0 wt%, and 1.50 wt%, of $Ti_3C_2T_x$, no new absorption peak appears and no obvious change to λ-max is observed. Even at 2.0 % wt of $Ti_3C_2T_x$, the UV–vis spectrum remained the same, indicating that additional MXene does not chemically react with V-Br$_3$ to generate new compounds. Small amounts of Mxene do not affect the positive electrolyte's redox reaction.

4.0 Conclusions

In conclusion, MXene's improved electrochemical properties are linked to the development of surface-active oxygen-containing functional groups C–O, C=O, and O– C=O, which can increase the active surface area and accelerate electron transfer and heat exchange properties of V-Br RFB. The thermophysical performance of the V-Br RFB is outstanding with different wt% of MXene-based VBr$_3$ electrolytes. Thermal conductivity increased by 75.9% with 2.0 wt% MXene at 45°C, whereas resistance dropped by 68.9%. Thermal diffusivity also increases as a result of this process. With high electrochemically stable and excellent thermal properties of V-Br RFB can be a good choice for large-scale energy storage.

5.0 References

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