Kastamonu University

Journal of Engineering and Sciences

e-ISSN 2667-8209

http://dergipark.gov.tr/kastamonujes

Synthesis and Characterization of Mn_3O_4 Doped Modified Electrodes for Vanadium Redox Flow Batteries

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ARTICLE INFO

Received: July:29.2019
Reviewed: October:4.2019
Accepted: October:10.2019

Keywords:
Vanadium redox flow battery,
Mn_3O_4/Vulcan XC-72,
Surface modification,
Graphite felt,
Carbon paper.

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ABSTRACT

In the present study, Mn_3O_4 doped electrodes were synthesized to improve the cathode V (IV)/V (V) redox reaction of all vanadium flow batteries. Cathode electrocatalysts were produced with a two-step hydrothermal method. The crystal structure of the Mn_3O_4 doped composites and electrodes were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) was used for morphological examination of the samples. Surface modification of the electrodes was confirmed by thermo gravimetric analysis (TGA) and functional groups on the electrode surface were determined by X-ray Photoelectron Spectroscopy (XPS). Electrochemical measurements of the electrodes were conducted with cyclic voltammetry (CV) technique. Mn_3O_4 directly loaded onto graphite felt and carbon paper and Mn_3O_4/Vulcan XC-72 nanocomposite increased the electrochemical catalytic activity of cathode V (IV) / V (V) redox reaction. Peak currents of Mn_3O_4/Vulcan XC-72 doped graphite felt and SGL 10AA electrodes are measured as 42.30 and 7.9 mA, respectively. Despite the low electrical conductivity of Mn_3O_4, the composites formed with Vulcan XC-72 improved vanadium flow battery cathode performance.

ÖZ

Anahtar Kelimeler:
Vanadyum redoks akış pili
Mn_3O_4/Vulcan XC-72
Yüzey modifikasyonu
Grafit keçe
Karbon kağıt

Bu çalışmada, oluşturulan Mn_3O_4 katkılı elektrotlar, vanadyum akış pilleri katot V(IV)/V(V) çifti için sentezlenmiştir. Katot elektrokatalizörleri iki aşamada hidrotermal yöntem kullanılarak sentezlendi. Elde edilen Mn_3O_4 katkılı kompozit ve elektrotların kristal yapısı X-ışını difraksiyonu (XRD), morfoloji incelemesi için ise taramalı elektron mikroskobu (SEM) kullanılmıştır. Yüzey modifikasyonu termo gravimetrik analiz (TGA) ile doğrulanmış olup yüzeydeki fonksiyonel gruplar X-ışını Fotoelektron Spektroskopisi ile tespit edilmiştir. Elektrotların elektrokimyasal ölçümleri çevrimsel voltametri (CV) kullnılarak yapılmıştır. İlk aşamada oluşturulan Mn_3O_4 /Vulcan XC-72 kompoziti ve ikinci aşamada grafit keçe ile karbon kağıt üzerine yüklenen Mn3O4 , katot V(IV)/V(V) çiftinin elektrokimyasal katalitik aktivitesini artırmıştır. Mn_3O_4 /Vulcan XC-72 katkılı grafit keçe ve SGL 10AA elektrotlarının çalışma akımları sırasıyla 42.30 ve 7.9 mA'dir. Mn_3O_4'ün düşük elektriksel iletkenliği olmasına rağmen Vulcan XC-72 ile oluşturulan kompozitler vanadyum akış pili katot performansını iyileştirmiştir.

1. Introduction

Renewable energy systems such as wind and solar systems are intermittent energy generating systems. In order for renewable energy sources to be sustainable and efficient to use, the energy produced must be stored and provided to the system when necessary. Energy storage systems (ESS) can store renewable energy in different forms and, if necessary, convert it back to electrical energy. When the energy storage system is in electrochemical form (e.g. batteries, fuel cells, flow batteries), energy can be stored efficiently, safe, and at a lower cost [1].

The use of redox flow batteries (RFB) that store energy in electrochemical form, in energy storage applications has become widespread in recent years [2]. As a result of the electrochemical reactions in the redox flow batteries, ions flow within the cell and electrons flow in the external circuit [3]. One major difference of flow batteries from secondary batteries such as Li-ion, Lead-Acid, Ni-Cd is that they do not store reactants or products in the cell, instead chemicals are stored in separate storage tanks. The energy capacity of the system increases with the amount of electrolyte (anolyte or catholyte) in the storage tanks. As the active electrode area increases, the current drawn from the cell increases. In addition, the voltage of the flow battery module can be increased with serial connection of the cells. Therefore, the ability to regulate power and energy capacities independently is one of the most important advantages of redox flow batteries.

Among redox flow batteries, vanadium redox flow battery (VRFB) is the most widely studied and developed cell type. As a result, VRFB flow batteries are commercially available and widely used worldwide. The VRFB was first studied by Maria Skyllas-Kazacos [4]. The cathode electrolytes (catholyte) contain V^{4+}/V^{5+} ions in H_2SO_4 solution, while the anode electrolyte (anolyte) consists of V^{3+}/V^{2+} ions in H_2SO_4 solution. The concentration, activity and stability of vanadium ions in electrolytes are critical for vanadium redox flow battery performance [5]. The energy density of a vanadium redox flow cell with an acidic electrolyte having a vanadium concentration of 2M is about 20-30 Wh/L. The low solubility of vanadium ions and cell voltage are the most important parameters affecting energy density [6]. When the flow battery is in discharge mode, V^{5+}/V^{4+} reduction reaction occurs on the cathode side while V^{2+}/V^{3+} oxidation reaction occurs on the anode side [7].

$$(1)\qquad \textbf{Cathode:}\ VO^{2+} + H_2O \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} VO_2^{+} + 2H^{+} + e^{-} \qquad E^{o}= 1.00V$$

$$(2)\qquad \textbf{Anode:}\ V^{3+} + e^{-} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} V^{2+} \qquad E^{o}=-0.25V$$

$$(3)\qquad \textbf{Cell:}\ VO^{2+} + H_2O + V^{3+} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} VO_2^{+} + 2H^{+} + V^{2+} \qquad E^{o}= 1.25V$$

Protons formed with the electrochemical reactions inside the electrodes are transferred from anode to cathode by means of proton conductive membrane to ensure charge balance in the cell. Carbon-based electrodes are generally used in a typical vanadium flow cell. Carbon electrodes are very advantageous in terms of proper surface area, low cost and anode-cathode stability[8]. Carbon paper, carbon cloth, graphite felt, and carbon fiber are the commonly used electrodes in flow battery systems. The precursor materials commonly used for the production of graphite felt fibers are polyacrylonitrile (PAN) or Rayon, affecting the physical and electrochemical properties of the graphite felt. Graphite felt obtained from PAN fibers shows better electrochemical properties as compared to Rayon based graphite felts [9]. Starting from the precursor material, graphite felt is produced by polymerization, oxidation, carbonization and graphitization processes respectively. In addition, graphite felt has high electroactive surface area, high electrical conductivity (370.37 S/m), good mechanical and chemical stability. On the other hand, the hydrophobic nature of the graphite felt limits performance in vanadium redox flow batteries [10,11]. Among the mentioned electrodes, to improve the weak electrochemical properties of the graphite felt electrode and to enhance the performance of the vanadium redox flow battery, surface modification should be carried out. Some methods used for surface modification are acid treatments [12], thermal treatments [13], thermo-chemical treatment, and hydroxylation [14]. As a result of the acid treatment of graphite felt with sulphuric acid, W. Zang and his coworkers reported that the oxygen-containing functional groups on the graphite felt surface increased. This increase in the surface of oxygen-containing functional groups increased the wettability of the graphite felt and reduced the resistance during charge transfer [15]. In general, precious metals such as Pt, Ru, Pd and Ir are used as electrocatalysts in Vanadium Redox Flow Batteries [16-18]. These precious metals significantly improve the performance of the VRFB, but the cost of these catalysts is quite high. In VRFB systems, instead of precious metals, low-cost metal oxide catalysts such as WO_3 [19] and Mn_3O_4 (referans) can be used. Due to its low electrical conductivity, Mn_3O_4 reduces the performance of vanadium redox flow battery by creating resistance during charge transfer. The performance of the vanadium redox flow battery can be increased when Mn_3O_4 is used as a composite with a porous material having good electrical conductivity. It is possible to obtain a catalyst with low cost, high conductivity and high electrochemical catalytic activity by providing homogeneous nano scale distribution of metal oxide catalyst in graphite felt electrode [20-22].

In this study, Mn_3O_4 metal oxide was used as catalyst. In order to improve the electrode kinetics, the low electrical conductivity of Mn_3O_4 was developed by impregnating onto the carbon black and the Mn_3O_4/Vulcan XC-72 composite was formed. To enhance the performance of the graphite felt electrode, surface modification was made using acid and thermal treatment methods. The produced Mn_3O_4/Vulcan XC-72 composite was placed in the graphite felt pores with the hydrothermal synthesis technique. X-ray diffraction (XRD), X-ray photo electron spectroscopy (XPS) and Scanning Electron Microscopy (SEM) techniques were used in the surface and structural analysis of the graphite felt obtained after surface modification with Mn_3O_4/Vulcan XC-72. Electrochemical measurements were performed by cyclic voltammetry tests.

2. Material and Method

2.1 Preparation of electrocatalyst

This study was carried out in two steps. In the first step, Mn_3O_4/Vulcan XC-72 electrocatalyst was prepared. Vulcan XC-72 (Cabot®) was treated with hydrogen peroxide (50%, Tekkim®) for surface activation at 120°C for 5h. The sample was washed with deionized water until the pH was stabilized and dried in a vacuum oven at 60°C overnight. Surface modified Vulcan XC-72 carbon was mixed in 1M $Mn(Ac)_2.4H_2O$ (99%, Sigma-Aldrich®) for 1h and after that sample was ultrasonicated for 3h. The graphite felt (3mm PAN based, Hi-Tech Carbon®) was cut to 3cm x 3cm. During the course of hydrothermal reaction, mixture of graphite felt electrode and Mn_3O_4/Vulcan XC-72 suspension was treated in a teflon coated autoclave for 12h at 200^{o}C. The autoclave was cooled to room temperature and the graphite felt electrode was washed with deionized water until pH was stabilized. The resulting graphite felt-based electrode was dried in a vacuum oven at 25^{o}C overnight. To compare Mn_3O_4 /Vulcan XC-72 performance, only Mn_3O_4 catalyst was loaded on the graphite felt by hydrothermal method. The Mn_3O_4/Vulcan XC-72 electrocatalyst was loaded on a carbon paper (10AA GDL, SGL Group®) by hydrothermal method to compare the graphite felt with carbon paper as an alternative electrode.

2.2 Characterization

Surface morphology analyses of the samples were performed using scanning electron microscopy (SEM) with an acceleration voltage of 10kV (JEOL, JSM-7001F). The X-Ray diffraction (RIGAKU, SMARTLAB) analyses of the samples were conducted using the Cu-Kα1 source with a screening angle of 2-90^o, and scanning speed of 2^o min^{-1}. Thermogravimetric analysis (TGA, BRUKER, TENSOR 27) was used to determine the thermal history of the electrodes. X-ray photoelectron spectroscopy (XPS) (PHI 5000 VersaProbe) was used to observe the functional groups on the surface of the electrodes.

2.3 Electrochemical measurements

Cyclic voltammetry (CV) analysis was performed with a scan rate of 5 mVs^{-1} in 0-1.5V range using 0.5M VO_SO_4 (99%, Sigma-Aldrich®) and 2M H_2SO_4 (95-97%, Merck®) solution. All electrochemical analyzes were performed under an inert atmosphere using a Potentiostat-Galvanostat (Stath, IVIUM) device and a standard three-electrode electrochemical cell. Ag/AgCl (3M NaCl) was used as the reference electrode and platinum wire was used as the counter electrode.

3. Result and Discussion

Fig.1 shows XRD patterns of graphite felt and carbon paper after surface modification of graphite felt and carbon paper with Mn_3O_4/Vulcan XC-72.

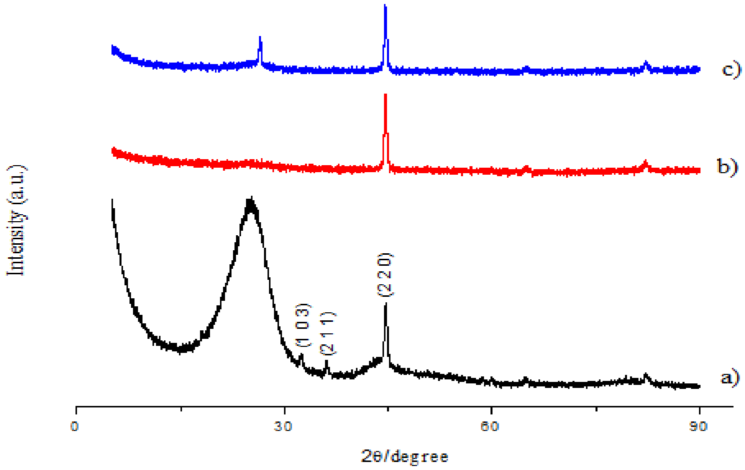
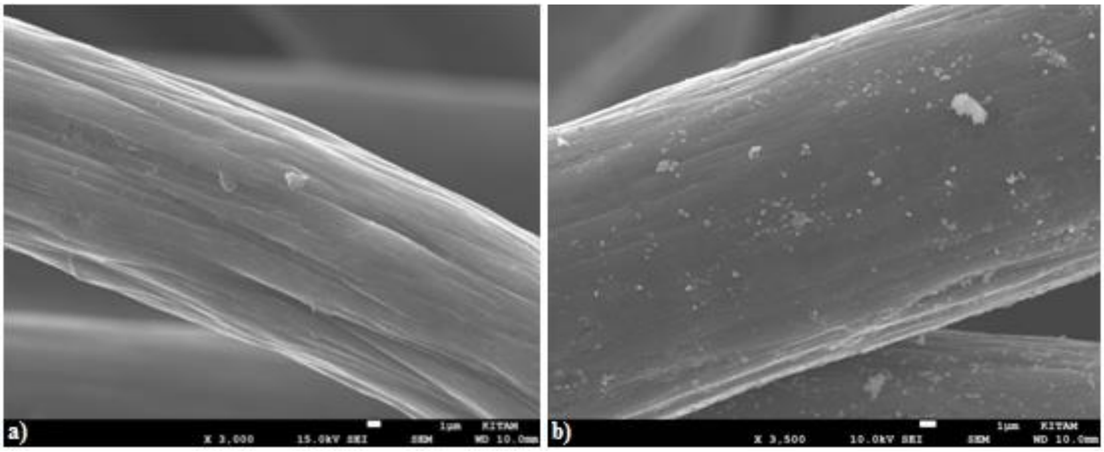


Figure 1. XRD paterns of electrodes **a)** Mn_3O_4/GF, **b)** Mn_3O_4+Vulcan XC-72/ GF, **c)** Mn_3O_4+Vulcan XC-72/10AA

In XRD analysis, a typical peak (002) was observed at 26.4° (JCPDS card files, no. 41-1487), which is generally attributed as the characteristic peak of the graphite felt and carbon paper. Observed diffraction peak positions and corresponding crystal planes of the Mn_3O_4 crystals on graphite felt and carbon paper are detected at 32.4° (1 0 3), 36.1° (2 1 1) and 44.5° (2 2 0) respectively. The resulting relatively low density diffraction peaks are in accordance with the reported values of Mn_3O_4. Crystallite size is related to the broadening of a peak in the diffraction pattern. The crystallite size of the Mn_3O_4 particle prepared by hydrothermal method was calculated using Scherrer formula and the average crystal size was found to be approximately 21 nm, which is in agreement with the reported data (Fig. 2c) in SEM micrograph [23].



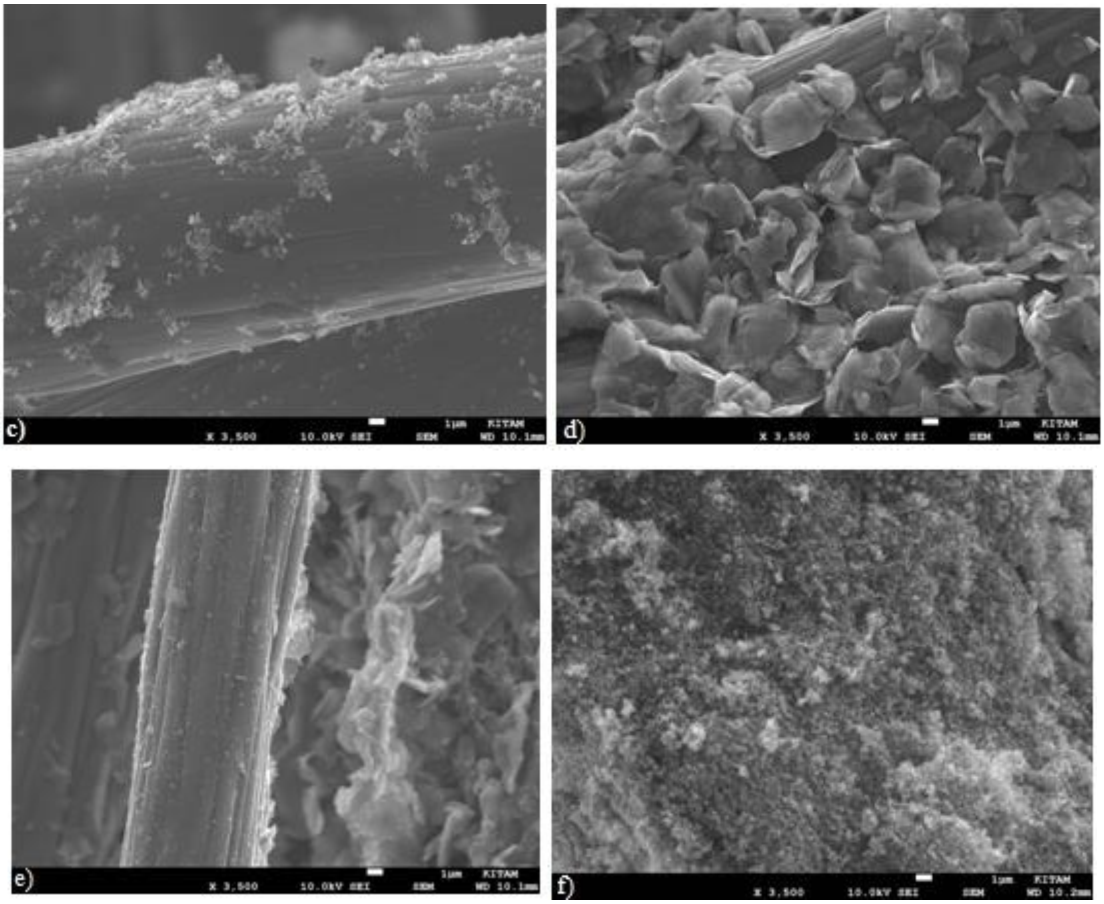


Figure 2. SEM images of electrodes **a)** pristine GF, **b)** Mn_3O_4 based GF, **c)** Mn_3O_4/Vulcan XC-72 based GF, **d)** pristine SGL 10AA**, e)** Mn_3O_4/Vulcan XC-72 based SGL 10AA, **f)** Mn_3O_4/Vulcan XC-72

The micrographs from the SEM analysis shown in Fig 2. exhibits the surface morphology of the Mn_3O_4 modified graphite felt electrode. When the SEM images are examined, it can be concluded that the Mn_3O_4 particles are successfully loaded onto the graphite felt.

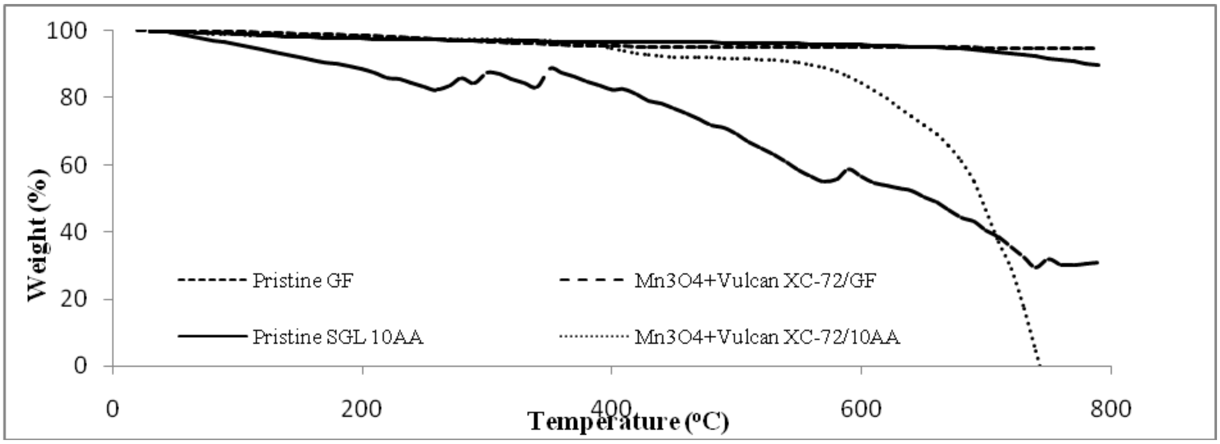


Figure 3. TGA curves of electrodes under nitrogen

The results of thermogravimetric analysis for graphite felt and carbon paper under nitrogen atmosphere before and after modification are shown in Fig.3. The mass loss of graphite felt and carbon paper after surface modification increased significantly. After the surface modification of electrodes, functional groups containing oxygen were possibly increased on the surface and, accordingly, these functional groups and small amounts of water on the surface were released during TGA analysis, resulting in an increase in mass loss in the electrodes. The increase in these functional groups increases the electroactive area on the surface, resulting in improved electrode kinetics in the vanadium redox flow batteries. TGA analyses showed that the pristine graphite felt and carbon paper remained thermally stable to the temperatures up to 800°C. 70% and 95% mass loss were observed on modified graphite felt and carbon paper, respectively. One may conclude that this mass loss supports the presence of functional groups containing oxygen on the electrode surface as a result of modification.

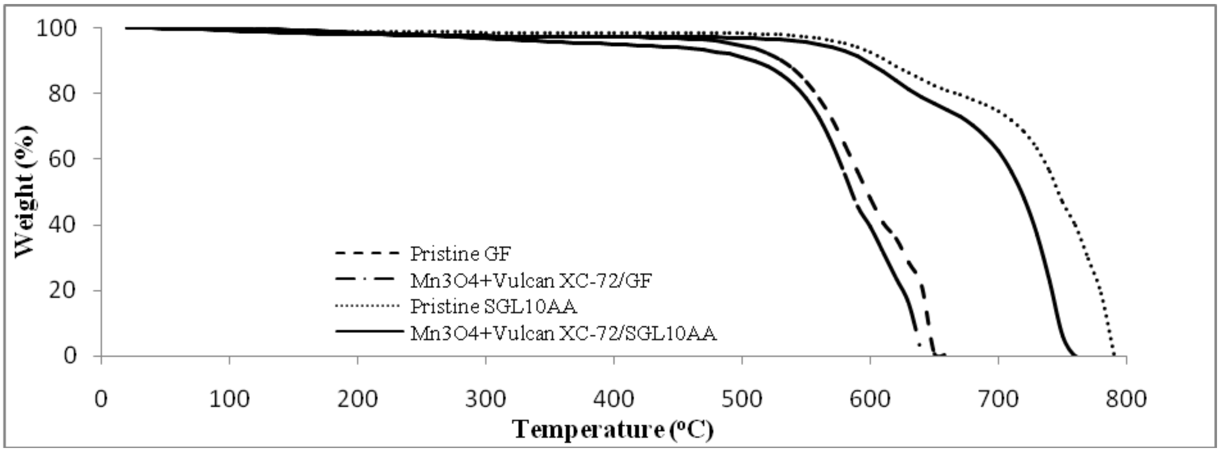
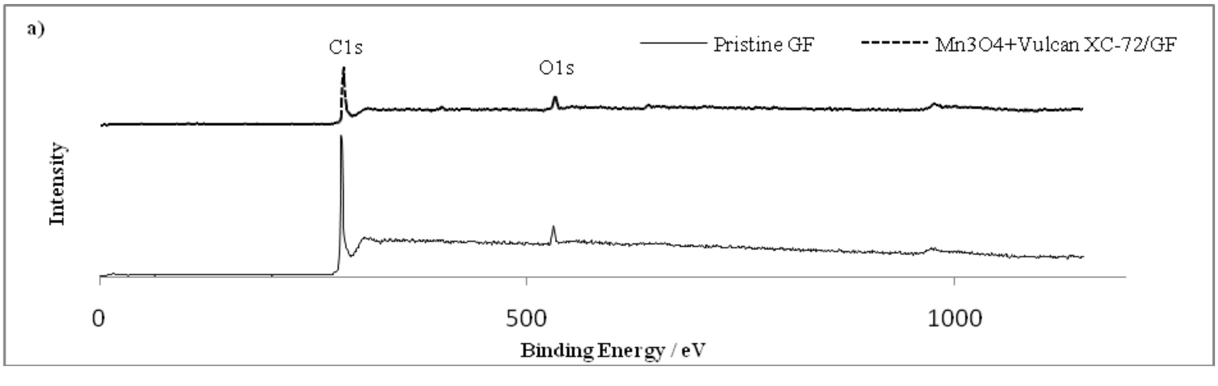


Figure 4. TGA curves of electrodes under air

The results of TGA analysis for graphite felt and carbon paper under oxygen atmosphere before and after modification are given in Fig. 4. Most of the mass loss is due to the combustion reaction of graphite felt and carbon paper in approximately 500 °C.

Fig. 5 shows the XPS surveys before and after graphite felt and GDL 10 AA are doped with Mn_3O_4/Vulcan XC-72.



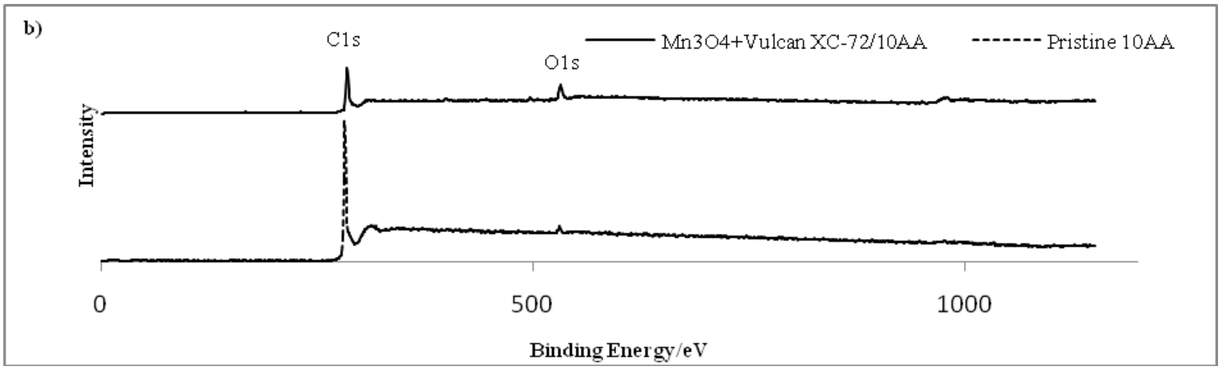
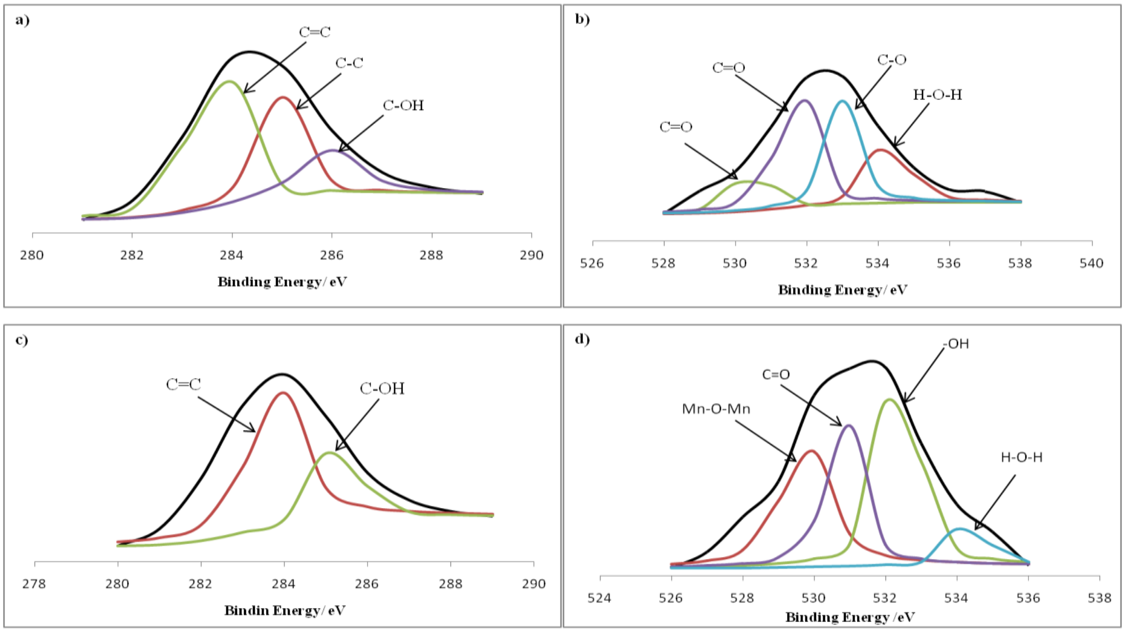


Figure 5. XPS surveys of 10AA and graphite felt

In addition, XPS data were used to fit a curve to get C1s and O1s spectra of all electrodes, which are presented in Fig. 6. Spectra are calibrated according to the binding energy of the carbon at 284.7 eV.



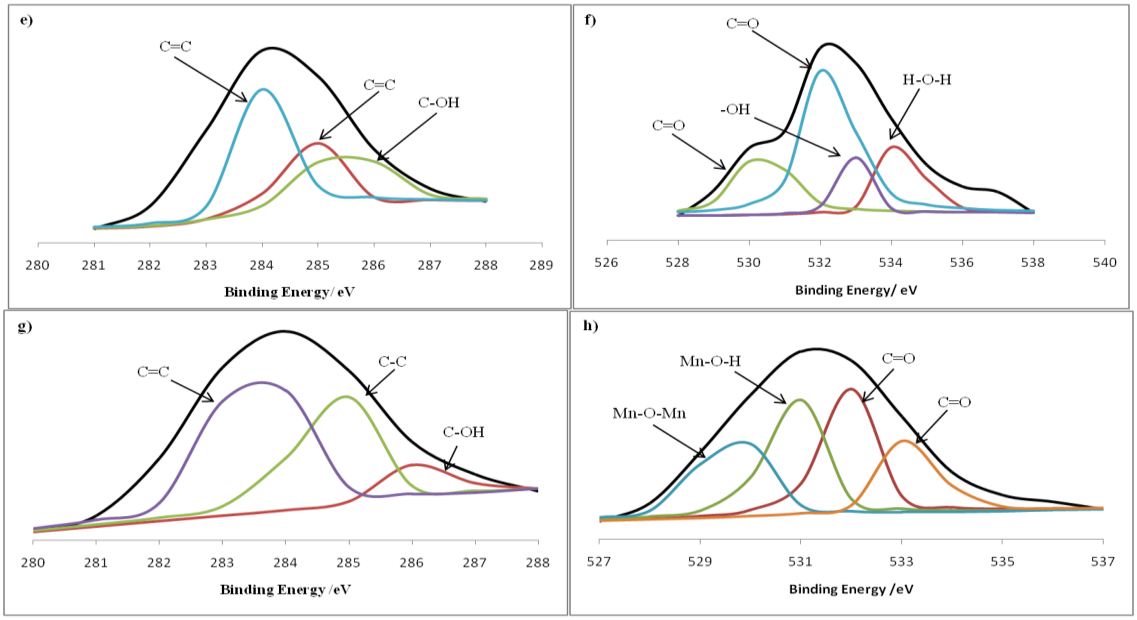


Figure 6. XPS curve-fit C1s and O1s spectra of electrodes, pristine GF (a and b) Mn_3O_4/Vulcan XC-72 based GF (c and d), pristine SGL 10AA (e and f), Mn_3O_4/Vulcan XC-72 based SGL 10AA (g and h)

The surface functional group contents of the samples are listed in Table 1 and Table 2. In Table 1, The O/C ratios of graphite felt and carbon paper were compared before and after modification. The O/C ratio was found as 0.15 and 0.17 for graphite felt and carbon paper, respectively, after modification. This result confirms the increase in functional groups containing oxygen on the electrode surface.

Table 1. XPS C1s and O1s spectra data

Sample	C1s (%)	O1s (%)	O/C Ratio
Pristine GF	95.30	4.70	0.05
Mn_3O_4+Vulcan XC-72/GF	87.25	12.75	0.15
Pristine SGL 10AA	98.60	2.40	0.02
Mn_3O_4+Vulcan XC-72/SGL 10AA	85.50	14.50	0.17

Table 2. Data of XPS functional groups

	C1s			O1s					
Sample	**C=C**	**C-C**	**C-OH**	**C-O**	**C=O**	**-OH**	**H-O-H**	**Mn-O-Mn**	**Mn-O-H**
Pristine GF	55.20	27.00	17.80	26,70	53		20.03		
Mn_3O_4+Vulcan XC-72/GF	49.92		25.63		23.68	36.84	8.60	27.65	
Pristine SGL 10AA	31.92	25.20	23.75		65.78	9.08	19.84		
Mn_3O_4+Vulcan XC-72/SGL 10AA	47.94	31.45	9.01		45.02			25.04	27.80

As can be seen from Fig.6, C1s peak positions and binding energies were attributed to C-C (284.7, 289.9 eV), C=C (283.75, 284 eV), C-OH (285.9, 286.25 eV) functional groups [24]. When the O1s peak positions and binding energies were examined, C-O (533 eV), C=O (530, 530.8, 531.7, 532.3 eV), -OH (532.88 eV), H-O-H (534.3, 534.4, 535 eV), Mn-O-Mn (529.7 eV), Mn-O-H (530.76 eV) functional groups were detected [25].

Fig. 7 and Fig. 8 show the cyclic voltammograms of graphite felt and SGL 10AA carbon paper electrode before and after surface modification.

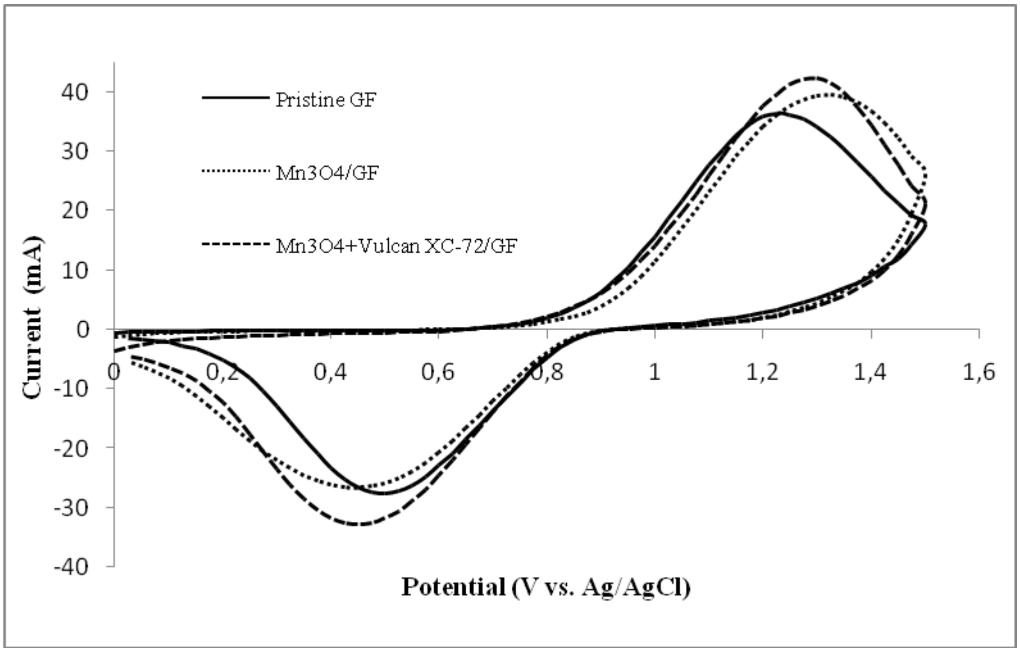


Figure 7. Cyclic voltammograms of graphite felt a scan rate of 5mVs^{-1} in 0,5 M $VOSO_4$+ 0,5 M H_2SO_4 solution

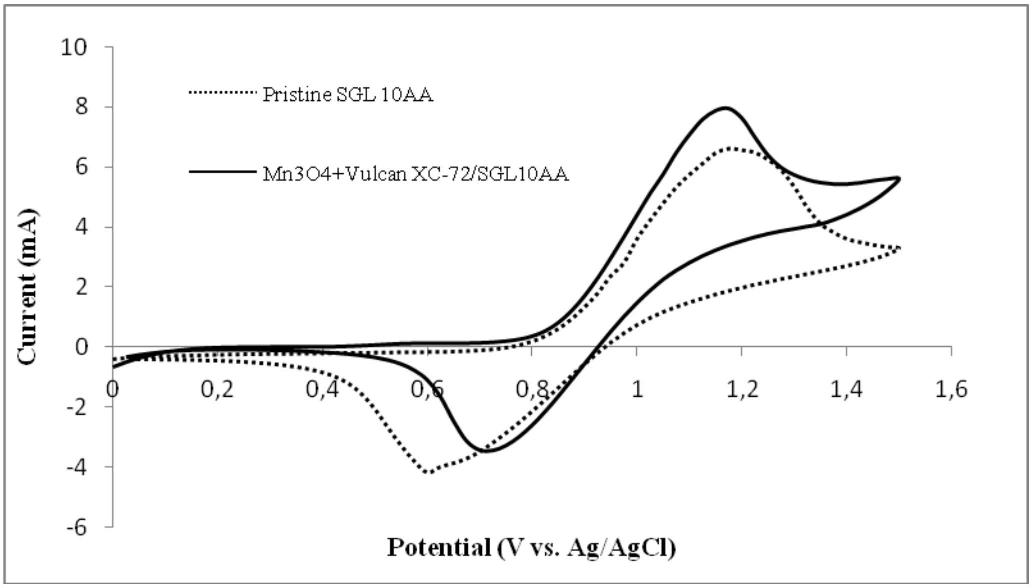


Figure 8. Cyclic voltammograms of SGL 10AA a scan rate of 5mVs^{-1} in 0,5 M $VOSO_4$+ 0,5 M H_2SO_4 solution

The data obtained from cyclic voltammograms are presented in Table 3 and Table 4.

Table 3. Parameters obtained from CV curves for graphite felt electrode

Electrode sample	I_{Pa} (mA)	E_{Pa} (V)	I_{Pc} (mA)	E_{Pc} (V)	I_{Pa}/I_{Pc}
Pristine GF	36.40	1.22	27.51	0.50	1.32
Mn_3O_4/GF	39.55	1.32	26.60	0.45	1.48
Mn_3O_4+Vulcan XC-72/GF	42.30	1.31	32.77	0.45	1.29

Table 4. Parameters obtained from CV curves for SGL 10AA

Electrode sample	I_{Pa} (mA)	E_{Pa} (V)	I_{Pc} (mA)	E_{Pc} (V)	I_{Pa}/I_{Pc}
Pristine Carbon Paper	6.61	1.17	4.15	0.60	1.59
Mn_3O_4+Vulcan XC-72/Carbon Paper	7.97	1.17	3.45	0.72	2.31

Cyclic voltammograms have good characteristic symmetry. The high performance of electrodes containing Mn_3O_4+Vulcan XC-72 is due to the active Mn_3O_4 electrocatalyst. When Mn_3O_4/GF and Mn_3O_4+Vulcan XC-72/GF were compared, it was determined that the best performance was obtained with Mn_3O_4+Vulcan XC-72 based graphite felt. This high performance is probably resulted from the homogenous distribution of the electrocatalyst by impregnating the Mn_3O_4 electrocatalyst with Vulcan XC-72 into the graphite felt. Activation of Vulcan XC-72 carbon black caused Mn_3O_4 crystals to retain in a more stable form on the carbon surface. Electrocatalyst impregnation with surface modification facilitates the transfer of electrons in the graphite felt to enable oxidation at the cathode. In addition, by increasing the wettability of the graphite felt, the transfer of vanadium ions was facilitated, which increased the V (IV)/V (V) cathode electrocatalytic performance.

4. Conclusions

In this study, Mn_3O_4 / Vulcan XC-72 composite was synthesized by using hydrothermal method. The performance of the synthesized composite was examined for V (IV)/V (V) redox reaction. The XRD pattern shows that Mn_3O_4 particles were successfully dpoed into the electrode structure. XPS results indicate the presence of functional groups on the electrode surface and confirmed the increase in oxygen containing functional groups over the surface. Mass loss seen in TGA results was attributed to functional groups containing oxygen. When the catalytic performance of the electrodes was examined, electrodes prepared with Mn_3O_4/Vulcan XC-72 composite exhibited higher performance than pristine electrodes. The Mn_3O_4/Vulcan XC-72 composite is a promising cathode catalyst for vanadium redox flow battery.

Acknowledgment

The authors are very grateful for XPS analysis carried out at METU central laboratory. We also would like to thank Black Sea Advanced Technology Research and Application Center (KITAM) at OMU for XRD, SEM and TGA analysis. Authors are also grateful for the partial support provided by OMU BAP project through grant 218 number PYO.MUH.1904.16.013.

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