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Investigation the Effects of Tetrahydrofuran and Dimethyl Sulfoxide on the Positive Electrolyte of Vanadium Redox Flow Battery

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Electrochemical impedance spectroscopy,
Tetrahydrofuran,
Dimethyl sulfoxide

Abstract: In this work, a comparative study was done to determine the effects of tetrahydrofuran and dimethyl sulfoxide on the electrochemical behaviors of a vanadium redox flow battery's (VRFB's) positive electrolyte. In this concept, cyclic voltammetry and electrochemical impedance spectroscopy were used for the characterization of electrolytes consisting of additives, V(IV) and sulfuric acid. Currents and capacities of peaks were determined in cyclic voltammograms. The redox reaction were controlled by diffusion and diffusion+adsorption in tetrahydrofuran and dimethyl sulfoxide including positive electrolyte solutions of VRFB, respectively. Resistance values were investigated in electrochemical impedimetric analysis. The morphological characterization of the pencil graphite electrodes used in cyclic voltammetric analysis, were done by scanning electron microscopic analysis.

Tetrahidrofuran ve Dimetil Sülfoksitin Vanadyum Redoks Akışkan Bataryadaki Pozitif Elektrolit Üzerine Olan Etkilerinin Araştırılması

Anahtar Kelimeler
Dönüşümlü voltametri,
Elektrokimyasal empedans spektroskopisi,
Tetrahidrofuran,
Dimetilsulfoksit

Özet: Bu çalışmada, tetrahidrofuran ve dimetil sülfoksitin vanadyum redoks bataryanın pozitif elektrolitinin elektrokimyasal davranışına olan etkilerinin karşılaştırılmalı bir çalışması yapılmıştır. Bu kapsamda, katkı maddesi, V(IV) ve sülfürik asit içeren elektrolit çözeltilerinin karakterizasyonu için dönüşümlü voltametri ve elektrokimyasal empedands spektroskopisi kullanılmıştır. Piklerin akım ve kapasiteleri voltamogramlardan elde edilmiştir. Redoks reaksiyonu tetrahidrofuran içeren pozitif elektrolit çözeltisinde difüzyonken ile kontrollü gerçekleşmişken, dimetil sulfoksit içeren çözeltide difüzyon+adsorbsiyon ile kontrollü olarak gerçekleşmiştir. Elektrokimyasal impedimetrik analizlerde ise direnç değerleri incelenmiştir. Voltametrik analizlerde kullanılan kalem ucu grafit elektrotun yüzey karakterizasyonu taramalı elektron mikroskobu analizleri ile yapılmıştır.

1. Introduction

Electrochemical energy storage devices has an important potential for storage of produced energy from many different sources such as solar, wind, water and etc., [1–5]. Flow battery systems can be used to storage of large amount of electric energy in chemical form [6, 7]. Vanadium redox flow battery (VRFB) is the most known flow battery systems. It was discovered in University of New South Wales. Long cyclic-life, low cost, safely use and environmentally friendly concepts of VRFB are the most known properties for the battery system [8–13].

Electrolytes, electrodes and membrane are the main components of a VRFB [14, 15]. Positive electrolyte (catholyte) and negative electrolyte (anolyte) solutions consist of V(II)-V(III) and V(IV)-V(V), respectively in sulfuric acid. [12]. The occurring redox reactions between vanadium species in positive and negative electrolyte solutions were given in Eq. 1 and Eq. 2, respectively [16].

The concentrations of vanadium and sulfuric acid have important effects on the capacity of the battery system [17]. Some organic and inorganic additives in the electrolytes were used to improve the performance of the battery [18–22]. However, there

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are still need for low cost and high performance additives for positive electrolyte of vanadium redox battery. In this concept, organic solvents can play important roles for improving electrochemical performance of the positive electrolyte of VRFB. Although tetrahydrofuran and dimethyl sulfoxide were used as solvents for non-aqueous flow battery, they were not being used as additives for vanadium redox flow battery [23, 24].

$$VO^{2+} + H_2O \xrightleftharpoons[\text{discharge}]{\text{charge}} VO_2^{+} + 2H^{+} + e^{-} \quad E^{o}= 1.00\ \text{V vs. NHE} \qquad (1)$$

$$V^{3+} + e^{-} \xrightleftharpoons[\text{discharge}]{\text{charge}} V^{2+} \quad E^{o}=-0.26\ \text{V vs. NHE} \qquad (2)$$

In this study, tetrahydrofuran and dimethyl sulfoxide were used as additives for positive electrolytes of vanadium redox battery. The electrolyte systems were characterized by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). Amount optimization of additives were done by using of electrochemical technics. Mass transfer mechanism were determined for each additives. The morphological changes on the surface of used electrodes in cyclic voltammetric analysis were determined by microscopic analysis. EDX analysis were carried out to determine the chemical composition of the used electrodes.

2. Experimental

2.1. Preparation of electrolytes

Positive electrolytes consisting of 2.0 M V(IV) were prepared by dissolving of $VOSO_4$ (>99%, Sigma-Aldrich) in 5.0 M of sulfuric acid. Different amount of organic solvents (tetrahydrofuran, THF and dimethyl sulfoxide, DMSO) were separately added as 1.0, 3.0, 5.0 and 10.0 v/v% in the positive electrolyte of VRB, respectively.

2.2. Electrochemical analysis

Electrochemical experiments were carried out in a classical three-electrode cell for the electrolyte systems. In cyclic voltammetric analysis, the potential was scanned from 0.45V to 1.45V versus saturated calomel electrode (SCE). Anodic and cathodic peak redox capacities were determined by calculating the areas of the peaks [16, 25]. Pencil graphite electrode (PGE), which had 0.1 cm^2 surface area, was used as working electrode. Counter electrode was platinum wire.

EIS analysis were done in open circuit potential. The frequency range was 10^5–10^{-2} at 10 mV amplitude voltage. Raw EIS spectra were fitted to given circuit model in Fig. 1 [26]. CV and EIS analysis were done with Reference 3000 Potentiostat/Galvanostat under room temperature.

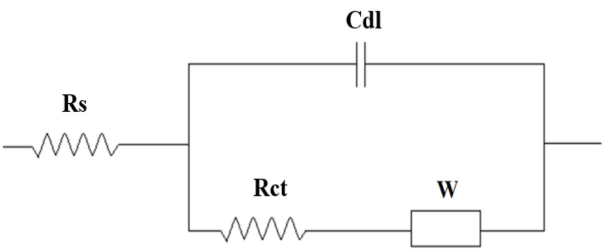

Figure 1. Used equivalent circuit model for fitting process [26, 27]

2.3. Microscopic characterization of electrodes

Structural changes on the surface of electrodes were determined by using of scanning electron microscopy. Analysis were done with Zeiss EVO® LS 10 model equipment. The electrodes were coated by Au at 40 sec. and 30 mA.

3. Result and Discussion

3.1. Electrochemical characterization of electrolytes

Cyclic voltammetric analysis were done to determine the effects of dimethyl sulfoxide as additive on the electrochemical behaviors of VRB's catholyte. Fig. 2a shows the cyclic voltammograms of electrolytes consisting of different amount (v/v % 1.0, 3.0, 5.0 and 10.0) of additives. Obtained oxidation and reduction peaks at around of 1.050 V and 0.850 V represent the oxidation of V(IV) to V(V) and reduction of V(V) to V(IV), respectively (Fig. 2a) [12, 28, 29]. When dimethyl sulfoxide was added into V(IV) solution as v/v% 1, currents and capacities of anodic and cathodic peaks decreased (Fig. 2b and 2c) [12, 26]. This result probably caused adsorption effects of used additive for active V(IV) species to the electrode surface due to less adsorption of active vanadium species to the electrode surface. When the ratio of additive as v/v% 3 in the electrolyte solution, the parameters were almost same with blank solution (Fig. 2b and 2c) [12, 16, 30]. The optimal adsorption was probably completed on the surface of electrode at this amount of additive. Besides, the diffusion of active V(IV) species to PGE surface was probably decreased due to interactions of DMSO molecules in the electrolyte solution [16, 30]. Although anodic and cathodic peak currents decreased in higher amount of additive than v/v% 3, the differences between anodic and cathodic peak potential decreased. This also supported catalytic effect of additive for the responsible redox reaction (Fig. 2d) [18, 31]. The mechanism of the mass transfer for the redox reaction was also determined by using of peak currents against the square root of the scan rates (Fig. 2e). Adsorption and diffusion process had a key role during the electrochemical reaction in the dimethyl sulfoxide including V(IV) solution on the PGE surface (Fig. 2e) [28].

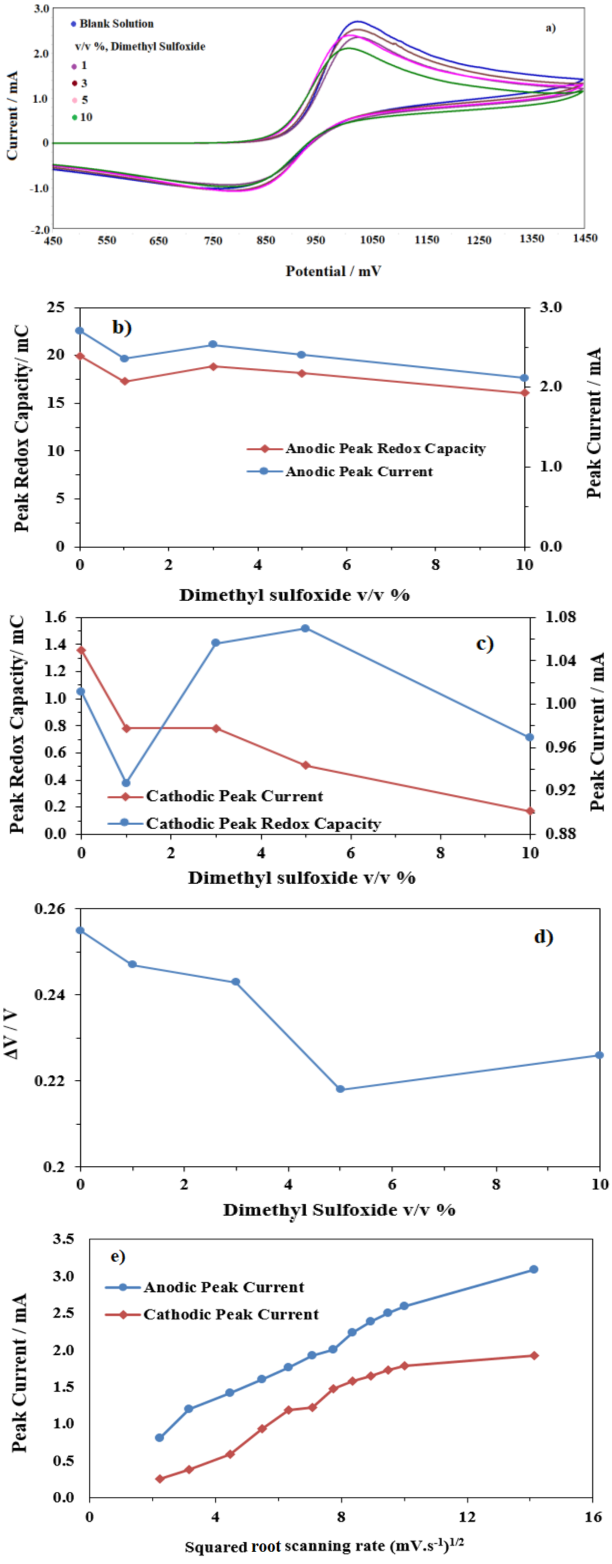

Figure 2. a) Cyclic voltammograms, b) capacities and currents of oxidation peak, c) capacities and currents of reduction peak, d) potential difference between oxidation and reduction peaks, and e) the plot of oxidation and reduction peak currents against the square root of the scan rates of PGE in positive electrolytes consisting of 2.0 M V(IV), 5.0 M sulfuric acid, and additive (different amount of dimethyl sulfoxide as v/v% 1.0, 3.0, 5.0 and 10.0)

EIS specta of solutions consisting of different amount of DMSO in catholyte solution of VRB were shown in Fig. 3. In fitted EIS spectra, ohmic resistance (Rs) also known as solution resistance and charge transfer resistance (Rct) were studied. Besides, Warburg impedance (W), which was related diffusion of mobile ion to the electrode surface, was investigated. Solution resistance of the electrolyte increased as function of increasing amount of additive due to limitation of mobility of ions in the electrolytes consisting of additive, as expected (Table 1) [12, 16, 30]. Rct values increased by adding of additives. Here, redox reaction occurred harder by increasing amount of additive. This result probably caused interactions of additive molecules and active vanadium species. Formed more stable form of vanadium species in the solution by adding of DMSO probably let low diffusion rate to the electrode surface (Table 1). Since the adsorption and diffusion play key role on the mass transfer mechanism for the redox reaction, formed species with additive particles and V(IV) species could bring another way for occurring redox reaction on the electrode surface which could also increase the activation energy of the reaction by increasing Rct values [16, 30]. Warburg impedance values also supported to this result. W values decreased by increasing amount of additive indication low diffusion rate (Table 1) [12, 16, 30]. Optimum amount of DMSO was chosen as v/v% 3 according to result of cyclic voltammetric and electrochemical impedance spectroscopic analysis.

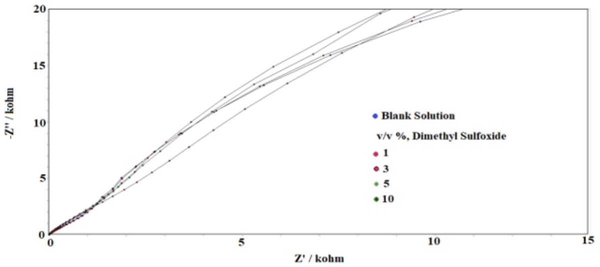

Figure 3. EIS spectra of PGE in electrolytes consisting of 2.0 M V(IV), 5.0 M sulfuric acid, and additive (different amount of dimethyl sulfoxide as v/v% 1.0, 3.0, 5.0 and 10.0)

Table 1. Rs, Rct, and W values of V(V) solutions consisting of 2.0 M V(IV), 5.0 M sulfuric acid, and additive (different amount of dimethyl sulfoxide as v/v% 1.0, 3.0, 5.0 and 10.0)

v/v % DMSO	Fitted EIS measurements results		
	Rs (ohm)	Rct (ohm)	W
0	1.739	1022	27.67 x 10^{-6}
1	1.959	1346	21.47 x 10^{-6}
3	2.237	1578	20.76 x 10^{-6}
5	2.247	1590	25.72 x 10^{-6}
10	2.562	1220	25.50 x 10^{-6}

Cyclic voltammograms of electrolytes consisting different amount (v/v%, 1, 3, 5 and 10) of tetrahydrofuran were shown in Fig. 4a. When the amount of additive was v/v% 1, currents and capacities of oxidation and reduction peaks increased (Fig. 4b and 4c). Besides, the difference of cathodic and anodic peak potential was the lowest in v/v% 1 tetrahydrofuran including solution of positive

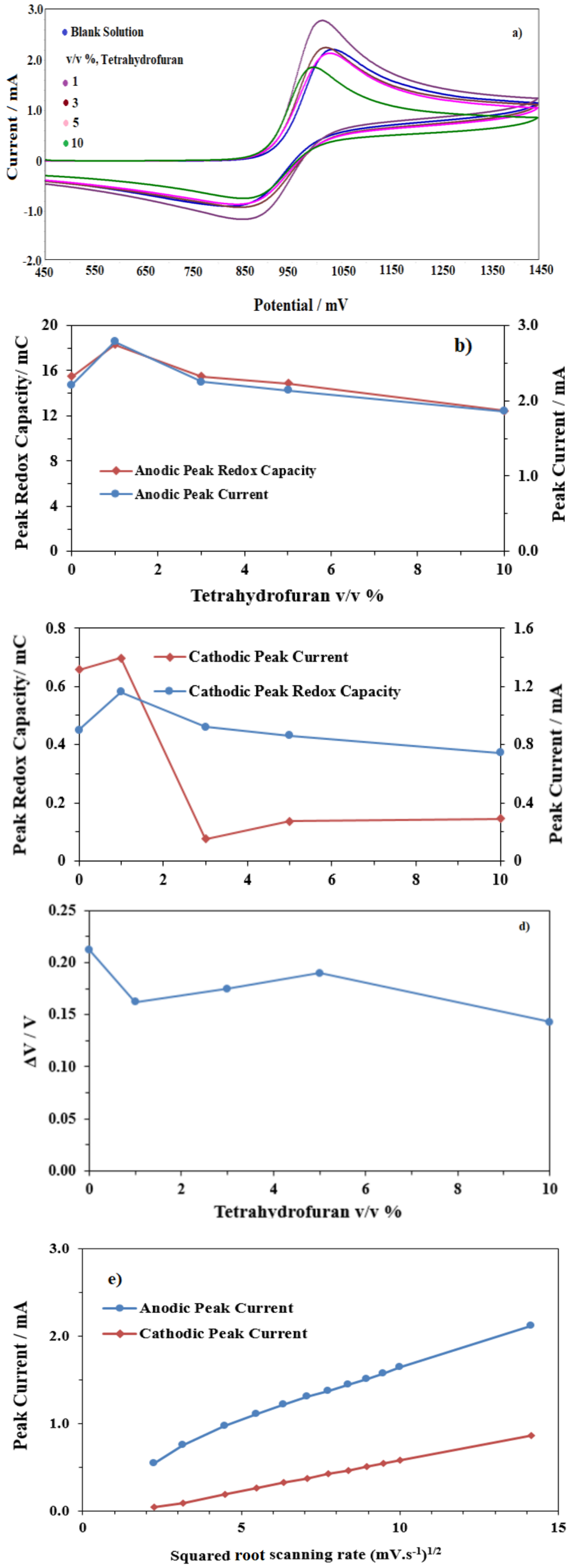

Figure 4. a) Cyclic voltammograms, b) capacities and currents of oxidation peak, c) capacities and currents of reduction peak, d) potential difference between oxidation and reduction peaks, and e) the plot of oxidation and reduction peak currents against the square root of the scan rates of PGE in positive electrolytes consisting of 2.0 M V(IV), 5.0 M sulfuric acid, and additive (different amount of tetrahydrofuran as v/v% 1.0, 3.0, 5.0 and 10.0)

electrolyte (Fig. 4d). The surface of electrode was activated well at this amount of additive. When higher amount of additive than optimum value was used in the solution, the interactions of additive and active V(IV) species probably increased and more stable form of vanadium species were formed in the electrolyte. This also limited the diffusion of V(IV) ions towards PGE surface. On the other hand, the main redox reaction was controlled by diffusion as mass transfer mechanism (Fig. 4e) [28]. This also limited the adsorption effect of additive for active V(IV) species to the electrode surface. So, currents and capacities of the oxidation and reduction peaks decreased in the solution consisting higher amount of THF than v/v% 1 (Fig. 4b and 4c).

Fig. 5 shows the EIS spectra of solutions including different amount of THF. Solution resistance of electrolytes decreased due to limited mobility of active ions in the solutions as a function of the increasing amount of organic solvent (Table 2) [12, 16, 30]. Charge transfer resistance decreased by the adding of additive indicating an easier pathway for the oxidation/reduction reactions as the effect of the additive (Table 2). The surface of PGE was probably modified by the molecules of additive. This also let an easy way for the oxidation and reduction reaction by forming intermediated species. The diffusion of the V(IV) ions towards the PGE surface increased by adding of tetrahydrofuran according to the W impedance value (Table 2). Optimum amount of THF was chosen as v/v% 1 for THF according to the results of electrochemical analysis.

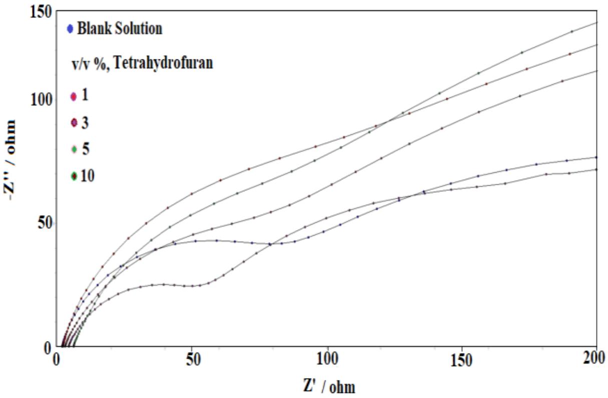

Figure 5. EIS spectra of PGE in electrolytes consisting of 2.0 M V(IV), 5.0 M sulfuric acid, and additive (different amount of tetrahydrofuran as v/v% 1.0, 3.0, 5.0 and 10.0)

Table 2. Rs, Rct, and W values of V(V) solutions consisting of 2.0 M V(IV), 5.0 M sulfuric acid, and additive (different amount of tetrahydrofuran as v/v% 1.0, 3.0, 5.0 and 10.0)

v/v % THF	Fitted EIS measurements results		
	Rs (ohm)	Rct (ohm)	W
0	1.933	242.9	2.04×10^{-3}
1	1.650	126.2	4.52×10^{-3}
3	3.720	100.2	5.10×10^{-3}
5	5.434	231.0	2.72×10^{-3}
10	6.559	244.2	2.95×10^{-3}

3.2. Morphological characterization of electrodes

Scanning electron microscope pictures were taken to investigate the structural changes of PGE during the cyclic voltammetric analysis in the electrolytes consisting of additives. The surface of bare PGE (Fig. 5a) changed during 10 voltammetric cycle in THF (PGE1) and DMSO (PGE2) including positive electrolyte of VRB in Fig. 5b and Fig. 5c, respectively. The graphitic layers can be seen clearly after voltammetric treatment. Besides, mass transfer was controlled by diffusion and diffusion+adsorption in the solutions including THF and DMSO additive, respectively according to the result of electrochemical analysis (Fig. 2e and Fig. 4e). The determined chemical composition by EDX analysis of the electrodes after voltammetric analysis supported this result. Although vanadium species were determined in DMSO including solution as additive, there was no peak for vanadium species in the solution consisting of THF as additive (Table 3).

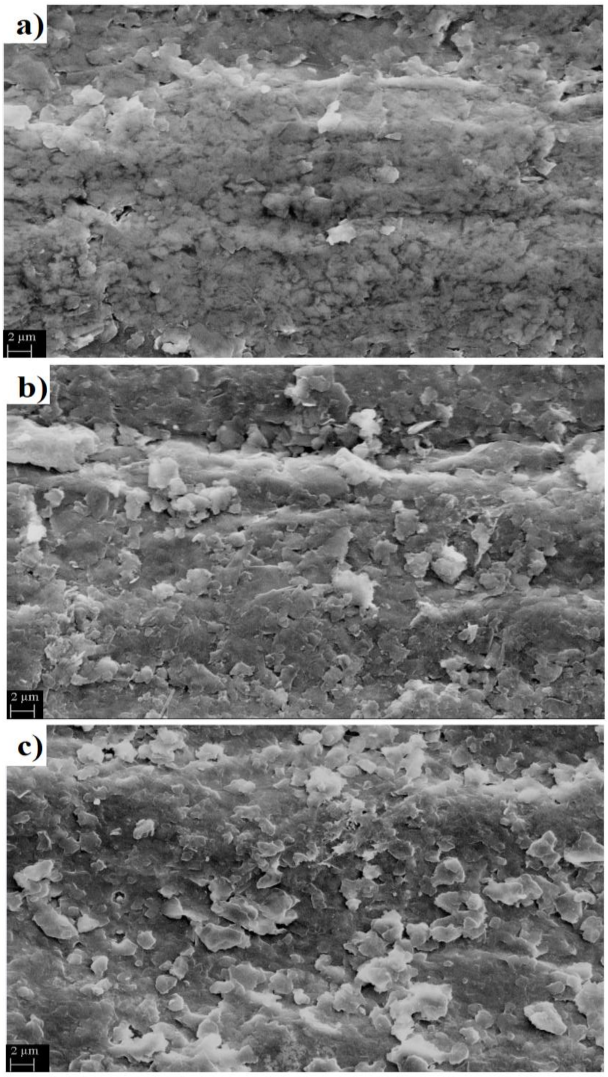

Figure 5. SEM pictures of PGE a) bare, b) after 10 voltammetric cycle in THF including V(IV) solution, and c) after 10 voltammetric cycle in DMSO including V(IV) solution

Table 3. Chemical composition of bare PGE, PGE1 and PGE2

Element	Bare PGE	PGE1	PGE2
	wt%	wt%	wt%
C	90	91	84
Si	7	4	3
O	3	3	7
S	-	2	5
V	-	-	1

4. Conclusion

In presented work, the effects of THF and DMSO on the electrochemical behaviors of V(IV) solutions of VRB. The electrolyte solution were characterized by electrochemical methods. Optimum amounts of additives were determined by electrochemical technics. They were v/v % 1 and v/v % 3 for THF and DMSO as additive to the electrolyte solutions. Mass transfer mechanism was also only diffusion in the THF including positive electrolyte solution. When the additive was DMSO, both of diffusion and adsorption were determined as mass transfer mechanism for the redox reaction. The morphological changes on the PGEs during the cyclic voltammetric analysis were also investigated by SEM and EDX analysis. The graphitic layers were seen easily after ten voltammetric cycle in the additives including electrolyte solutions. According to the results, THF and DMSO can be suggested as positive electrolyte additives for vanadium redox flow battery.

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