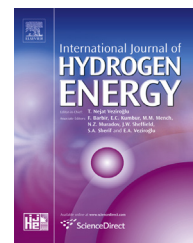


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# Electrochemical investigation of the effects of V(V) and sulfuric acid concentrations on positive electrolyte for vanadium redox flow battery

Metin Gençten <sup>a,b</sup>, Hürmüs Gürsu <sup>c,d</sup>, Yücel Şahin <sup>c,\*</sup>

<sup>a</sup> Anadolu University, Faculty of Science, Department of Chemistry, 26470 Eskişehir, Turkey

<sup>b</sup> Ordu University, Faculty of Arts & Science, Department of Chemistry, 52200 Ordu, Turkey

<sup>c</sup> Yildiz Technical University, Faculty of Arts & Science, Department of Chemistry, 34220 Istanbul, Turkey

<sup>d</sup> HMY Chemistry & Energy Ltd. Company, Çiftelavuzlar mah., Eski Londra Asfaltı Cad. 151/1G B2 Blok No: 137, 34220 Esenler, Istanbul, Turkey

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## ABSTRACT

In this study, the concentration effects of sulfuric acid solution and V(V) on positive electrolyte component of vanadium redox batteries were investigated by cyclic voltammetry and electrochemical impedance spectroscopy with pencil graphite working electrode for the first time. The current and redox capacity values of the oxidation and reduction peaks were determined by cyclic voltammetry. The optimum scanning rate and sulfuric acid concentration were at 20 mV s<sup>-1</sup> and 5.0 M, respectively. The current and capacity values of the anodic and cathodic peaks were found to increase but the charge transfer resistance decreased with increasing sulfuric acid concentration. When the concentration of V(V) was increased from 0.04 M to 2.0 M, the current and capacity values of the anodic and cathodic peaks increased. The charge transfer resistance also decreased with increasing the concentration of V(V), as expected.

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## Introduction

Renewable energy sources have great potential for sustainable energy production around the world [1]. Since the researchers are focused on these sources, production and storage of this energy become an important issue. Conventional batteries such as lead-acid, Li-ion, Ni–Cd and NiMH can be used for storage of this energy however there is still a need for alternative energy storage systems [2].

Vanadium redox battery (VRB), consisting of vanadium ions at different oxidation state in sulfuric acid solutions inside of both cell, is new generation energy storage system which was discovered and employed in University of New South Wales (UNSW) for the first time [3–6]. Since it has many advantages such as high energy efficiency (up to 80%), simple control and monitoring systems, long cyclic life, high safety, relatively low cost of maintenance, flexible design and environmental friendship, VRB has been a good alternative and

\* Corresponding author. Department of Chemistry, Faculty of Arts & Science, Yildiz Technical University, 34210 Istanbul, Turkey. Tel.: +90 212 3834411; fax: +90 212 3834134.

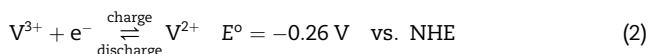
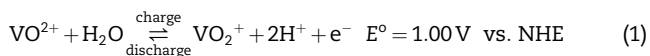
E-mail address: [yucelsahin06@gmail.com](mailto:yucelsahin06@gmail.com) (Y. Şahin).

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used many energy storage application [7–11]. Electrolytes, membrane and electrodes are the main components of VRB systems [12].

In electrolytes, concentrations of vanadium ions and sulfuric acid are significant parameters for the energy density of VRB system [13]. The redox reaction between V(IV)/V(V) (Eq. (1)) and V(III)/V(II) (Eq. (2)) occurs in positive and negative electrolyte solutions on electrode surface, respectively [8].



Most of studies about electrolyte component of VRB were focused on positive electrolyte and thermal stabilizing of V(V) ion at high temperature since it precipitated as  $\text{V}_2\text{O}_5$  by increasing temperature ( $>40^\circ\text{C}$ ). Electrochemical characterization of positive electrolyte solutions was an important part of these studies [8,14–18]. Oriji et al. (2005) was investigated V(II)/V(III) and V(IV)/V(V) redox reactions by cyclic voltammetry and potentiostatic polarization method with glassy carbon working electrode in high concentrations of sulfuric acid and vanadium species [19]. The concentration effects of sulfuric acid (1–9 M) solutions having  $2.0 \text{ mol L}^{-1} \text{ VOSO}_4$  was also studied by cyclic voltammetry with rotating disc electrode [20]. However, different concentrations of vanadium species were not studied by electrochemical methods. Electrochemical behaviors of graphite-based electrodes were also studied by Kim (2011). The redox reactions of V species and gas evolutions ( $\text{O}_2$  and  $\text{H}_2$ ) potential were determined by cyclic voltammetry [21]. Wen et al. (2006) was used a graphite rod electrode to determine concentration effects of V(IV) and sulfuric acid by cyclic voltammetry, low speed linear polarization and electrochemical impedance spectroscopy [22]. Although concentration effects of vanadium species were studied, concentrated V(V) solutions instead of V(IV) were not investigated in this work. Besides, sulfuric acid effects were studied only for 1–4 M solutions and optimization of scanning rate for cyclic voltammetric measurements was not studied. Since V(V) ion is vital parameter for vanadium redox battery systems, electrochemical characterization of solutions having different concentration of V(V) ion and sulfuric acid by novel electrodes is still needed to search.

In this work, electrochemical characterization of positive electrolyte solutions consisting of different concentration of V(V) and sulfuric acid was investigated with pencil graphite electrode (PGE) for the first time. Anodic and cathodic peak currents and peak redox capacities were examined by cyclic voltammetry (CV). Optimum scanning rate was determined as  $20 \text{ mV s}^{-1}$  for cyclic voltammetric studies. Current and redox capacity values of anodic and cathodic peaks were higher by the time concentrations of sulfuric acid and V(V) were increased. Solution resistance ( $R_s$ ) and charge transfer resistance ( $R_{ct}$ ) values were studied by electrochemical impedance spectroscopy (EIS).  $R_s$  values were found to decrease by increasing concentration of sulfuric acid up to 5.0 M. There was no change in the  $R_s$  values above this sulfuric acid concentration.  $R_{ct}$  also decreased by increasing concentration of

$\text{H}^+$  and  $\text{SO}_4^{2-}$  ions. Optimum concentration of sulfuric acid was determined as 5.0 M. When the concentration of V(V) ion increased from 0.04 M to 2.0 M,  $R_{ct}$  showed a certain decrease. The highest value of  $R_s$  was obtained in the solution consisting of 0.5 M V(V) and 5.0 M sulfuric acid.

## Experimental

Positive electrolytes, containing 0.2 M of V(V), were prepared with 1.0; 2.0; 3.0; 4.0; 5.0 and 6.0 M of sulfuric acid (Sigma–Aldrich,  $>95.0$ – $98.0\%$ ). 0.04; 0.08; 0.12; 0.16; 0.20; 0.50; 1.0 and 2.0 M of V(V) solutions were also prepared by electrolytic dissolution of  $\text{V}_2\text{O}_5$  (Aldrich,  $>99.6\%$ ) in 5.0 M sulfuric acid [4]. The concentrations of sulfuric acid and V(V) were determined by potentiometric titrimetric and UV-spectroscopic method, respectively [4,18].

Cyclic voltammetric and electrochemical impedance spectroscopic measurements were carried out with a classical three electrode system. In all electrochemical experiments, PGE having  $0.1 \text{ cm}^2$  geometrical surface area, saturated calomel electrode (SCE) and Pt wire were used as working, reference and counter electrode, respectively. Cyclic voltammetric measurements were performed between 0.45 and 1.45 V versus SCE with  $20 \text{ mV s}^{-1}$  scanning rate at room temperature. Electrochemical impedance spectra of electrolytes were obtained at open circuit potential over a  $10^5$ – $10^{-2} \text{ Hz}$  frequency range at an amplitude of 10 mV. The spectra were fitted an equivalent circuit model which was showed in Fig. 1 [16]. All the electrochemical experiments were carried out using a CHI Potentiostat/Galvanostat model 660D (CH Instruments, USA).

The structural features of the electrodes were examined with field emission scanning electron microscope using Carl Zeiss Ultra Plus FESEM. The change of PGE surface was investigated after a voltammetric cycle. The composition of electrode surfaces was determined an EDX (Oxford Instruments, INCA Energy) detector.

## Results and discussion

### Determination of scanning rate and mass transfer mechanism

Cyclic voltammetric measurements were performed between 0.45 and 1.45 V (vs. SCE) with PGE. The obtained anodic and cathodic peaks in this potential range represent the conservation of V(IV)/V(V) and V(V)/V(IV), respectively [21]. The cyclic

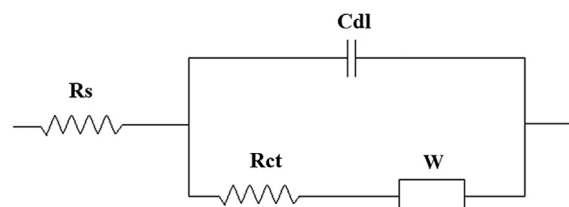


Fig. 1 – Equivalent circuit model.

voltammograms, obtained with different scanning rate (5; 10; 20; 30; 40; 50; 60; 70; 80; 90; 100; 200; 300; 400 and 500  $\text{mV s}^{-1}$ ) in solution consisting of 0.2 M V(V) and 5.0 M sulfuric acid, were given in Fig. 2a. When current and capacity values of anodic and cathodic peaks were plotted as a function of scanning rate, optimum scanning rate was determined as 20  $\text{mV s}^{-1}$  (Fig. 2b and c). Since the reversibility of redox reaction was investigated well at this scanning rate, it was chosen for further studies. The anodic and cathodic peak currents obtained cyclic voltammograms (Fig. 2b and c) were plotted against the square root of the scan rates and it was shown in Fig. 2d. A non-linear behavior was seen in plotted values (Fig. 2d). This result may be caused that the reaction was controlled by a charge transfer step as well as mass transfer step [21].

When the potential was scanned between 0.45 and 1.45 V (vs. SCE) in sulfuric acid solution, the graphitic surface of pencil graphite was activated by oxygen including functional groups such as hydroxyl and carboxylic acid [23]. The morphological change of graphite surface after one voltammetric cycle can be seen easily with different magnitudes in Fig. 3. Non-porous structure of graphite (Fig. 3a, c and e) changed and graphitic flake including porous structure was gained after one cycle (Fig. 3b, d and f). Besides, amount of oxygen increased and vanadium was determined after one cycle on the surface of PGE according the result of SEM-EDX analysis (Table 1). This result showed that vanadium species in the solution were adsorbed on the electrode surface while the redox reaction was occurring on PGE. Since adsorption of V(V) ions was higher on the activated surface of PGE, mass transfer step was determined even lower concentration of V(V) (0.2 M). The results let us to propose a reversible reaction

mechanism for V(IV)/V(V) and V(V)/V(IV) redox reactions on PGE surface (Fig. 4) [15,24].

### Optimization of sulfuric acid concentration

In this part of the study, the effect of sulfuric acid concentration on the performance of the positive electrolyte component of VRB was investigated by cyclic voltammetry and electrochemical impedance spectroscopy. Cyclic voltammetric measurements were performed in solutions consisting of different concentration of sulfuric acid (1.0; 2.0; 3.0; 4.0; 5.0 and 6.0) and 0.2 M of V(V) with PGE working electrode (Fig. 3a). The peak potentials of oxidation and reduction approached to each other in higher sulfuric acid concentrations (Fig. 5a). The similar behaviors were reported in literature for peak potentials [20,25]. This result can be explained by increasing reversibility of reaction in high acid concentration. Besides, the interactions of ions ( $\text{SO}_4^{2-}$ ,  $\text{H}_3\text{O}^+$ ) and PGE may increase the adsorption of V(V) ions [21]. In addition, the graphitic surface of PGE was more activated by oxygen including functional groups in concentrated sulfuric acid solution (6.0 M) than diluted acid solutions (1.0 M) [23]. This let to show a regular increase in the determined parameters by cyclic voltammetry. When the concentration of sulfuric acid was increased from 1.0 M to 6.0 M, current and capacity values of anodic and cathodic peaks were enhanced regularly (Fig. 5b). Since the reduction of V(V) to V(IV) occurs in acidic medium, increasing concentration of hydronium provides the reversibility of reduction reaction (Eq. (1)). As a result of the reversible redox reaction mechanism for positive electrolyte component on the surface of PGE, cathodic peak current and redox capacities also showed a regular increase (Fig. 5c). The

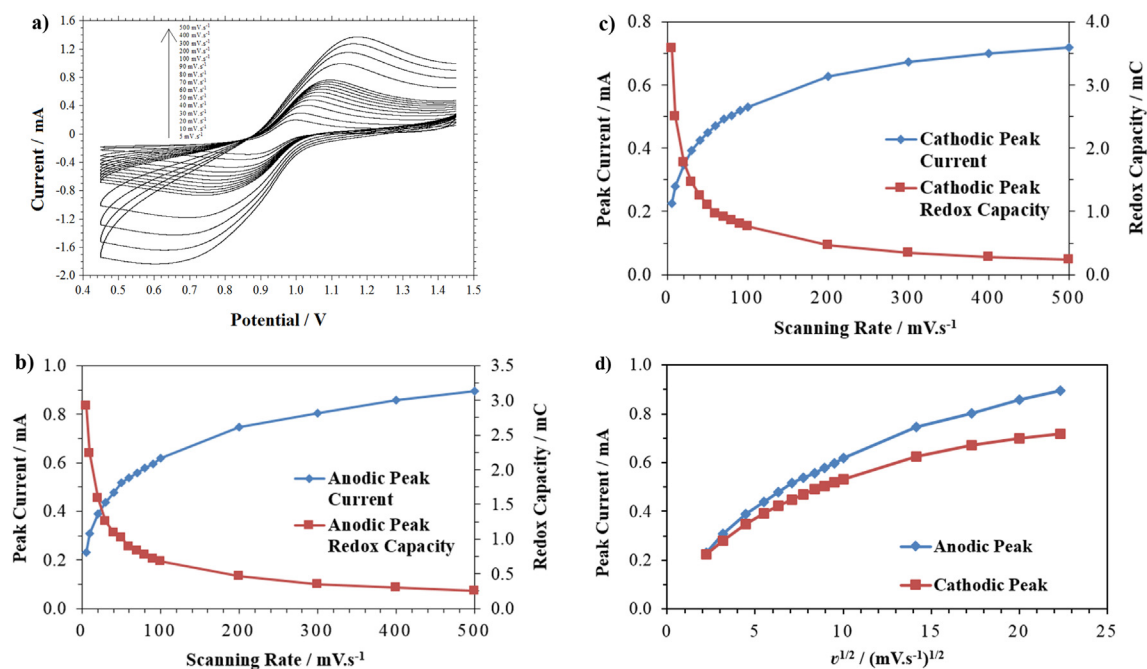
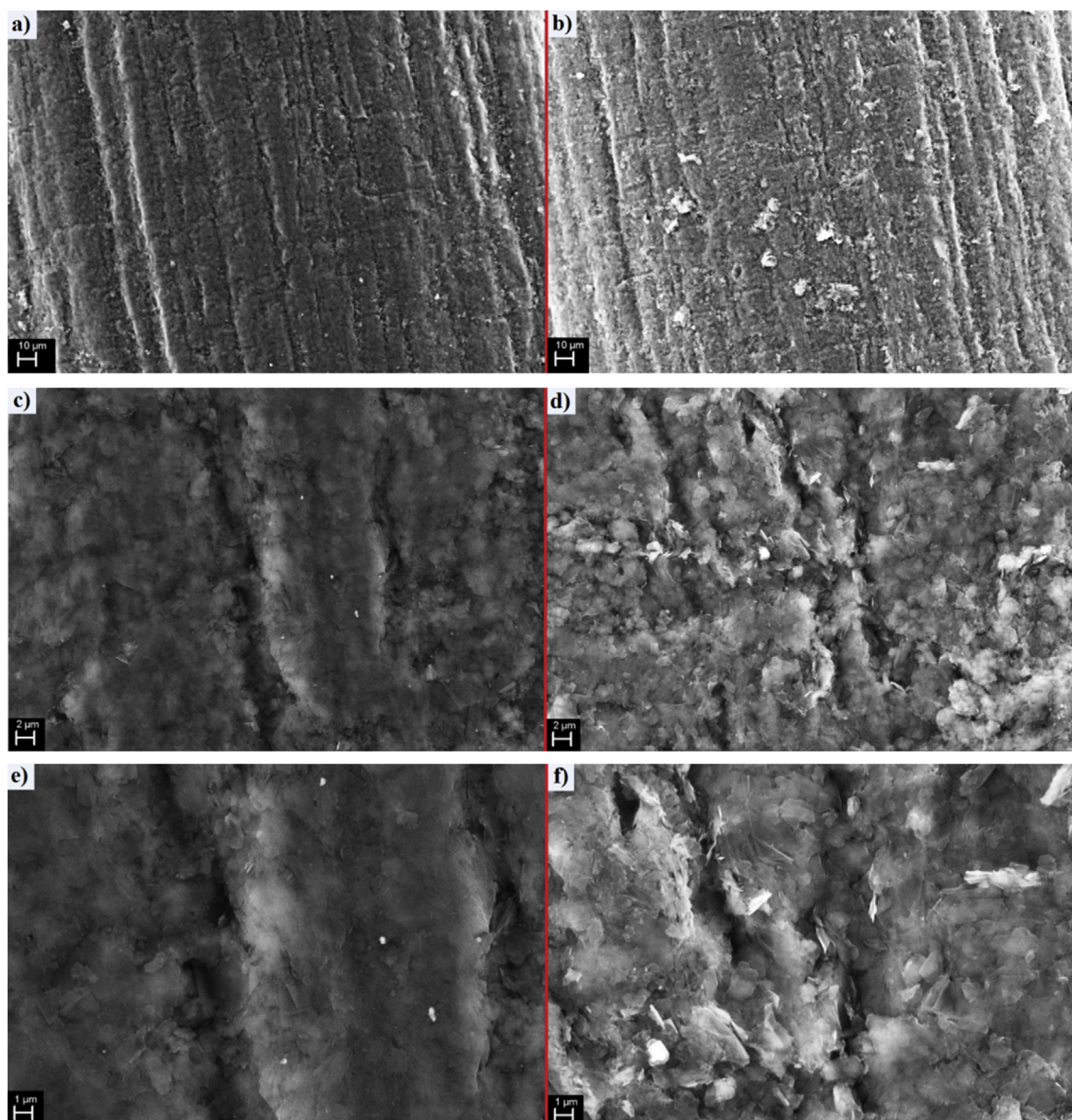


Fig. 2 – Cyclic voltammetric behaviors of PGE in electrolytes consisting of 0.2 M V(V) and 5.0 M sulfuric acid at different scanning rate a) cyclic voltammograms b) the anodic peak capacities and currents c) the cathodic peak capacities and currents d) plot of anodic and cathodic peak against the square root of the scan rates.





**Fig. 3 – SEM pictures of electrodes a) 1000 × magnitude of PGE b) 1000 × magnitude of PGE after one cycle c) 5000 × magnitude of PGE d) 5000 × magnitude of PGE after one cycle e) 10000 × magnitude of PGE f) 10000 × magnitude of PGE after one cycle.**

optimum concentration of sulfuric acid was determined as 5.0 M, because the PGE was deformed in more concentrated solutions. An extra oxidation peak (at 1.4 V) was obtained in solution consisting of 6.0 M (or higher) sulfuric acid. The peak

could be related forming dimer form of V(V) as  $V_2O_3^{4-}$  in concentrated sulfuric acid solutions [26].

Electrochemical impedance spectra of solutions having different concentrations of sulfuric acid are shown in Fig. 6a. Here,  $R_s$  and  $R_{ct}$  parameters represent solution resistance and charge transfer resistance, respectively.  $R_s$  shows the ohmic resistance having the resistance of electrolyte, the resistance of the corrosion products located on the surface of electrode, and the resistance of the electrical connections to the electrode.  $R_{ct}$  is related to the charge transfer resistance of the rate-controlling electrochemical reaction of corrosion process [22,27–29].  $R_s$  values decreased up to 4.0 M of sulfuric acid solutions, and then they were almost stable about 3.0 ohm (Fig. 6b). Since the mobility of ions was limited with excess amount of supporting electrolyte ( $H_2SO_4$ ),  $R_s$  values and

**Table 1 – Surface composition of PGE and PGE (after one voltammetric cycle).**

Element	PGE Weight%	PGE (After one voltammetric cycle) Weight%
C	93.86	87.04
O	3.71	10.29
Si	2.43	0.81
S	–	1.56
V	–	0.29

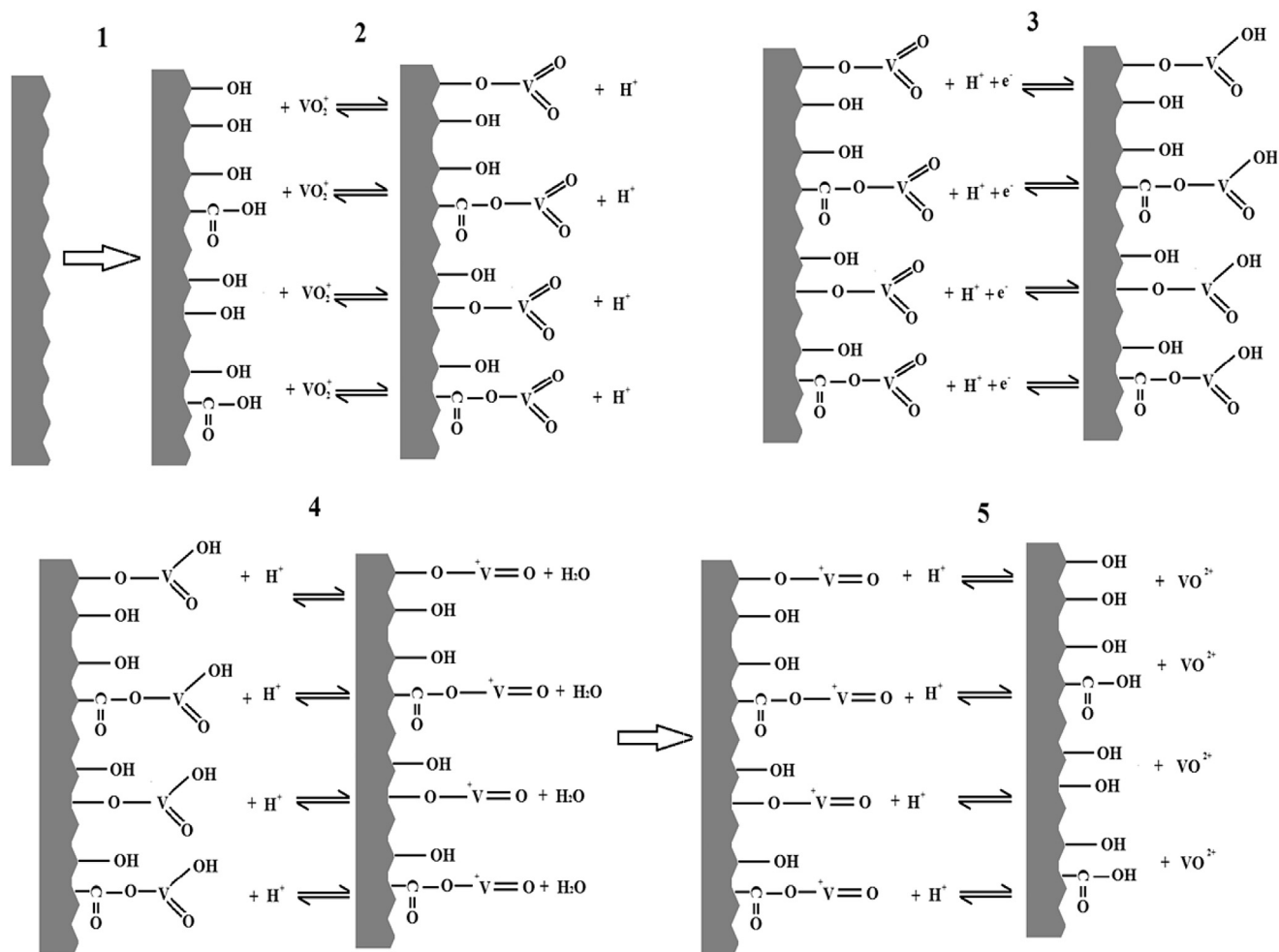


Fig. 4 – A plausible reaction mechanism of reversible V(IV)/V(V) redox reaction on PGE surface.

conductivity of solutions showed stable behaviors in 4.0, 5.0 and 6.0 M of sulfuric acid solutions [22,27]. Rct value had a sharp decrease in solution consisting 2.0 M of sulfuric acid (Fig. 6b). While Rct was about 4500 ohm in 1.0 M sulfuric acid solution, it was about 500 and 40 ohm in 2.0 and 6.0 M sulfuric acid solution, respectively. Since the amount of ions ( $\text{H}_3\text{O}^+$ ,  $\text{SO}_4^{2-}$ ) were increased in concentrated sulfuric acid solution, electron transfer between electrode surface and vanadium species was carried out easier than diluted acid solution (Eq. (1)) [27]. Rct values are very compatible with cyclic voltammetric results. When Rct values decreased, anodic and cathodic peak currents and redox capacities increased (Figs. 5b, c and 6b).

#### The effects of V(V) concentration

Concentration effects of V(V) ion were investigated by cyclic voltammetry and electrochemical impedance spectroscopy. In this concept, the electrolyte solutions were prepared consisting of different concentrations (0.04; 0.08; 0.12; 0.16; 0.20; 0.50; 1.0 and 2.0) of V(V) in 5.0 M of sulfuric acid solution. The cyclic voltammograms of solutions are given in Fig. 5a. The anodic and cathodic peak current and redox capacities increased in the solution having concentration of V(V) from 0.04 M to 2.0 M (Fig. 7b and c). When amount of V(V) ions was

higher in solution, the diffusion of ions was occurred higher on the surface of PGE. Besides, adsorption of ions on the electrode surface enhanced with increasing amount of vanadium species. This was also increased peak currents and redox capacities of anodic and cathodic peaks. Since the difference of anodic and cathodic peak potential increased with enhanced amount of V(V) ions, the reversibility of redox decreased [22].

The electrochemical impedance spectra of solutions consisting of different concentration of V(V) ions are given in Fig. 8a. Solution resistance was almost stable about 2.5 ohm up to solution having 0.2 M of V(V). When the concentration of V(V) was 0.5 M, Rs showed a sharp increase (Fig. 8b). This result may be explained by increasing viscosity and decreasing conductivity of solution consisting of higher concentration of V(V) (Fig. 8b) [22]. Rct values decreased with increasing amount of V(V) (Fig. 8b). This result was related with diffusion the higher amount of ions to the electrode surface. Besides, higher amount of V(V) was adsorbed on the electrode surface. The electron transfer from vanadium species to electrode surface occurred easier by increasing amount of V(V) in solution. Obtained Rct values were much appropriated to anodic peak currents and peak redox capacities (Figs. 7b, c and 8b).

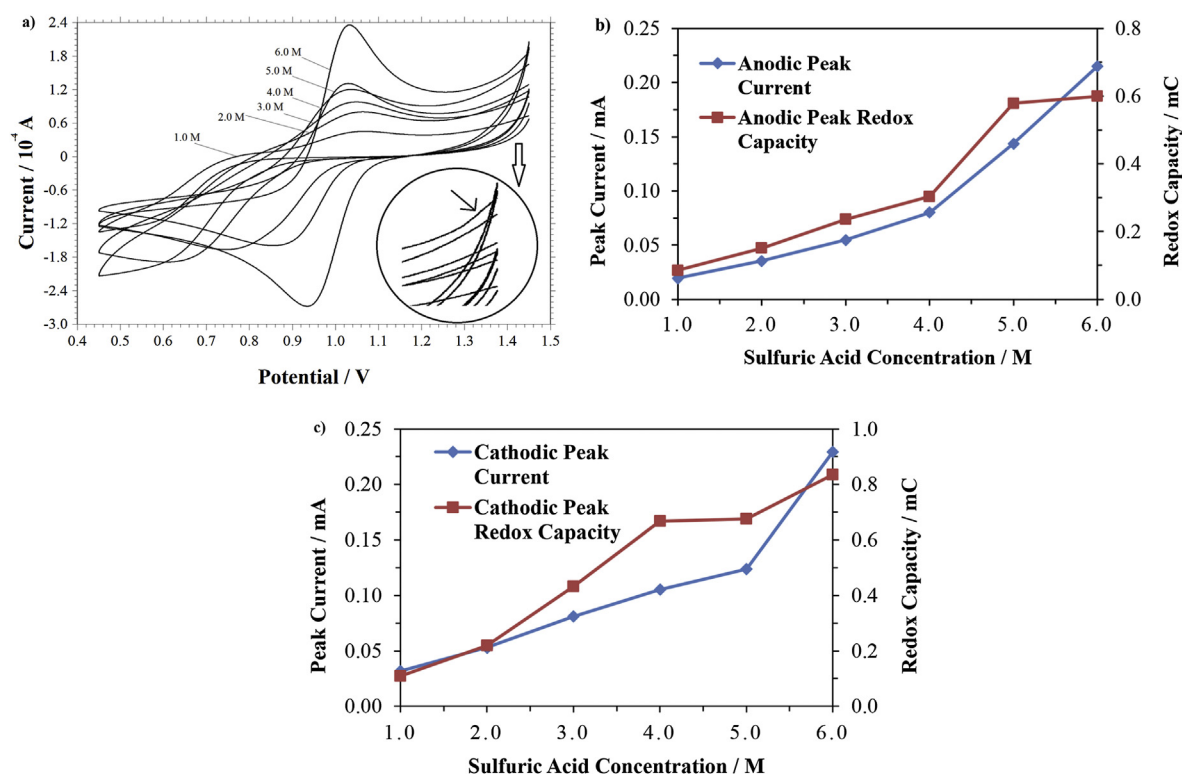


Fig. 5 – Cyclic voltammetric behaviors of PGE in electrolytes consisting of 0.2 M V(V) and different concentration sulfuric acid at 20 mV s<sup>-1</sup> scanning rate a) cyclic voltammograms b) the anodic peak capacities and currents c) the cathodic peak capacities and currents.

## Conclusions

Concentration effects of V(V) and sulfuric acid were investigated by using pencil graphite electrode for the first time in this work. While peak current and peak redox capacity values were examined by cyclic voltammetry,  $R_s$  and  $R_{ct}$  values were determined by electrochemical impedance spectroscopy for the solution having different concentration of V(V) and sulfuric acid. The optimum scanning rate was

determined as 20 mV s<sup>-1</sup> using data obtained by cyclic voltammograms. The mass transfer from solution to electrode surface was enhanced two steps; adsorption and diffusion. The optimum concentration of sulfuric acid was determined as 5.0 M. The anodic and cathodic peak currents and redox capacities were enhanced with increasing concentration of sulfuric acid. When the concentration of sulfuric acid solution was 6.0 M or higher, the structure of PGE was deformed and an extra oxidation peak was determined.  $R_s$  values were found to decrease up to solution having

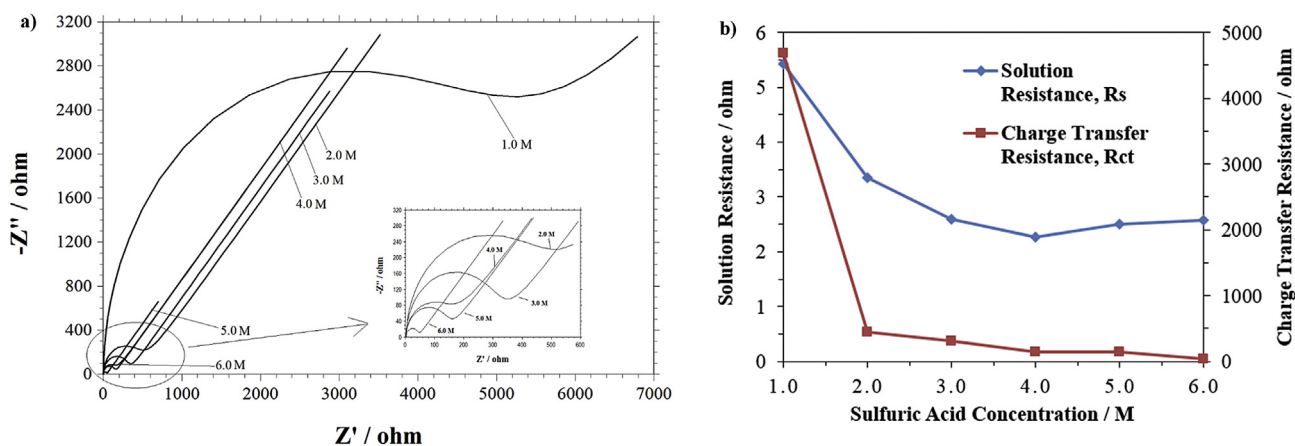
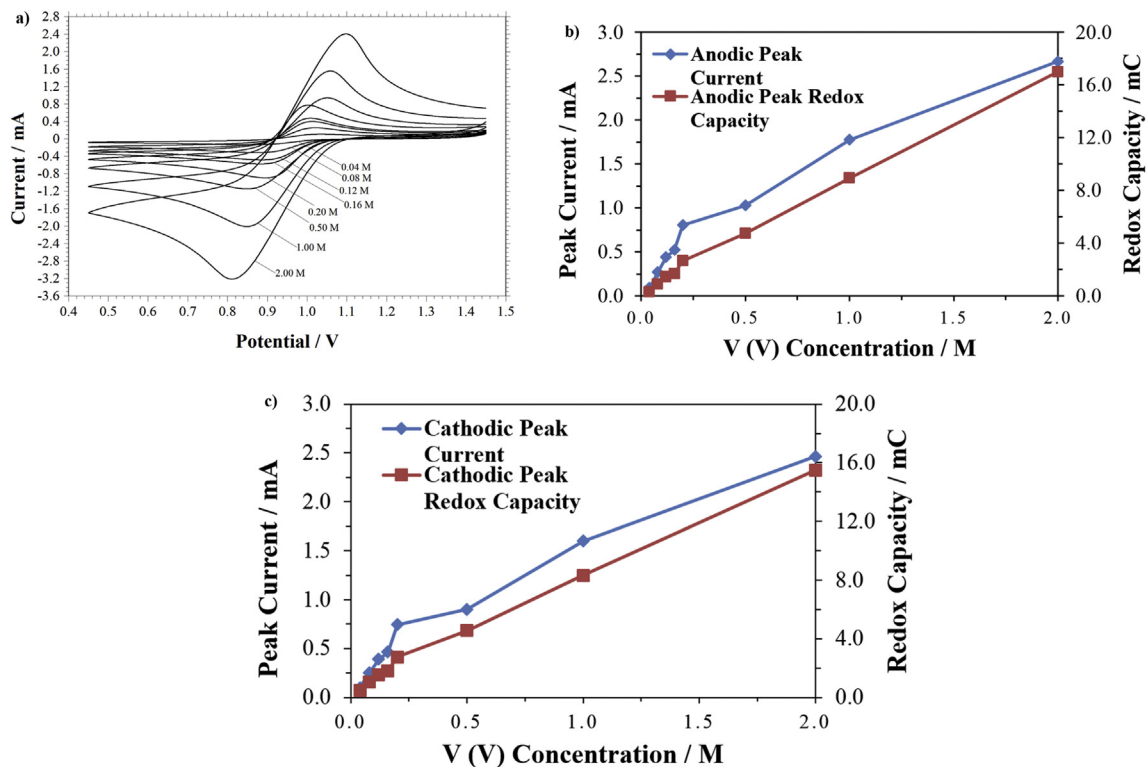
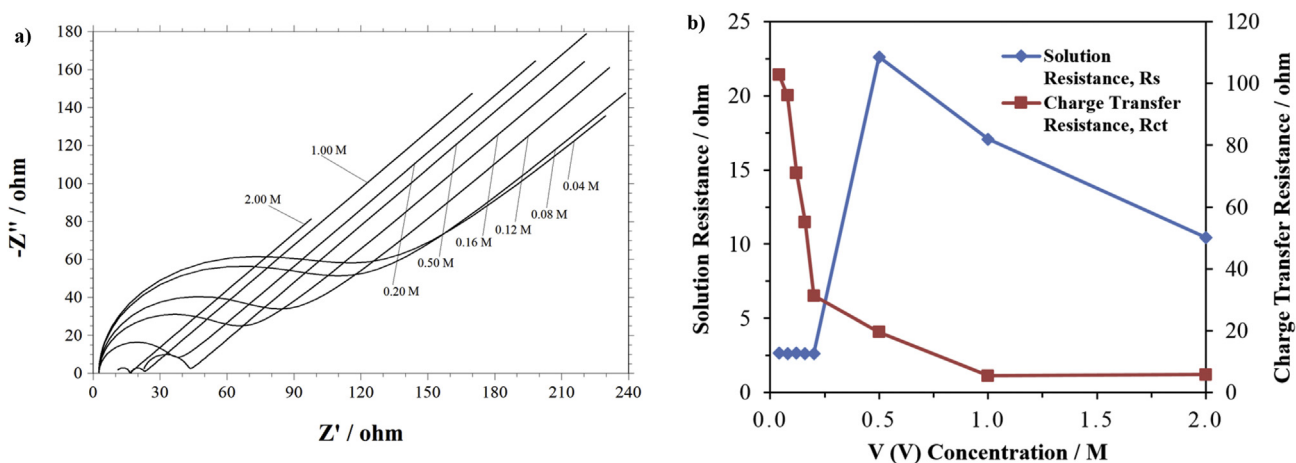


Fig. 6 – Electrochemical impedimetric behaviors of PGE in electrolytes consisting of 0.2 M V(V) and different concentration sulfuric acid a) impedance spectra b)  $R_s$  and  $R_{ct}$  values.



**Fig. 7** – Cyclic voltammetric behaviors of PGE in electrolytes consisting of 5.0 M sulfuric acid and different concentration of V(V) at  $20 \text{ mV s}^{-1}$  scanning rate a) cyclic voltammograms b) the anodic peak capacities and currents c) the cathodic peak capacities and currents.



**Fig. 8** – Electrochemical impedimetric behaviors of PGE in electrolytes consisting of 5.0 M sulfuric acid and different concentration of V(V) a) impedance spectra b)  $R_s$  and  $R_{ct}$  values.

3.0 M of sulfuric acid, and then it showed a stable behavior.  $R_{ct}$  values also decreased with increasing concentration of sulfuric acid as expected. The concentrated V(V) solution was an important parameter for VRB systems. Since adsorption mechanism was determined as mass transfer, currents and redox capacities of oxidation and reduction

peaks were increased in the solutions having higher concentration V(V) ions. When the concentration of V(V) was enhanced from 0.04 to 2.0 M,  $R_s$  values increased. Charge transfer resistance also decreased with increasing concentration of V(V). As a result, electrochemical characterization of electrolytes which have different concentrations of V(V)



and sulfuric acid can give useful information for the performance of VRB battery.

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## REFERENCES

- [1] Bilgili M, Ozbek A, Sahin B, Kahraman A. An overview of renewable electric power capacity and progress in new technologies in the world. *Renew Sust Energ Rev* 2015;49:323–34.
- [2] Subburaj AS, Pushpakaran BN, Bayne SB. Overview of grid connected renewable energy based battery projects in USA. *Renew Sust Energ Rev* 2015;45:219–34.
- [3] Sum E, Rychcik M, Skyllas-Kazacos M. Investigation of the V(V)/V(IV) system for use in the positive half-cell of a redox battery. *J Power Sources* 1985;16:85–95.
- [4] Kazacos M, Cheng M, Skyllas-Kazacos M. Vanadium redox cell electrolyte optimization studies. *J Appl Electrochem* 1990;20:463–7.
- [5] Skyllas-Kazacos MS, Robins RG. All-vanadium redox battery. U.S. Patent No. 4,786,567, 1988.
- [6] Skyllas-Kazacos M, Kazacos M, McDermott R. Patent application PCT appl/AKU 88/000471, 1988.
- [7] Skyllas-Kazacos M, Kazacos M. State of charge monitoring methods for vanadium redox flow battery control. *J Power Sources* 2011;196:8822–7.
- [8] Rahman F, Skyllas-Kazacos M. Vanadium redox battery: positive half-cell electrolyte studies. *J Power Sources* 2009;189:1212–9.
- [9] Ha S, Gallagher KG. Estimating the system price of redox flow batteries for grid storage. *J Power Sources* 2015;296:122–32.
- [10] Cunha Á, Martins J, Rodrigues N, Brito FP. Vanadium redox flow batteries: a technology review. *Int J Energy Res* 2015;39:889–918.
- [11] Alotto P, Guarnieri M, Moro F. Redox flow batteries for the storage of renewable energy: a review. *Renew Sust Energ Rev* 2014;29:325–35.
- [12] Parasuraman A, Lim TM, Menictas C, Skyllas-Kazacos M. Review of material research and development for vanadium redox flow battery applications. *Electrochim Acta* 2013;101:27–40.
- [13] Skyllas-Kazacos M, Peng C, Cheng M. Evaluation of precipitation inhibitors for supersaturated vanadyl electrolytes for the vanadium redox battery. *Electrochim Acta* 1999;44:121–2.
- [14] Liang X, Peng S, Lei Y, Gao C, Wang N, Liu S, et al. Effect of L-glutamic acid on the positive electrolyte for all-vanadium redox flow battery. *Electrochim Acta* 2013;95:80–6.
- [15] Li S, Huang K, Liu S, Fang D, Wu X, Lu D, et al. Effect of organic additives on positive electrolyte for vanadium redox battery. *Electrochim Acta* 2011;56:5483–7.
- [16] Wu X, Liu S, Wang N, Peng S, He Z. Influence of organic additives on electrochemical properties of the positive electrolyte for all-vanadium redox flow battery. *Electrochim Acta* 2012;78:475–82.
- [17] Chang F, Hu C, Liu X, Liu L, Zhang J. Coulter dispersant as positive electrolyte additive for the vanadium redox flow battery. *Electrochim Acta* 2012;60:334–8.
- [18] Park S, Shim J, Yang JH, Jin C, Lee BS, Lee Y, et al. Effect of inorganic additive sodium pyrophosphate tetrabasic on positive electrolytes for a vanadium redox flow battery. *Electrochim Acta* 2014;121:321–7.
- [19] Oriji G, Katayama Y, Miura T. Investigations on V(IV)/V(V) and V(II)/V(III) redox reactions by various electrochemical methods. *J Power Sources* 2005;139:321–4.
- [20] Oriji G, Katayama Y, Miura T. Investigation on V(IV)/V(V) species in a vanadium redox flow battery. *Electrochim Acta* 2004;49:3091–5.
- [21] Kim HS. Electrochemical properties of graphite-based electrodes for redox flow batteries. *Bull Korean Chem Soc* 2011;32:571–5.
- [22] Wen Y, Zhang H, Qian P, Zhao P, Zhou H, Yi B. Investigations on the electrode process of concentrated V(IV)/V(V) species in a vanadium redox flow battery. *Acta Phys Chim Sin* 2006;22:403–8.
- [23] Choo H, Kinumoto T, Jeong S, Iriyama Y, Abe T, Ogumi Z. Mechanism for electrochemical oxidation of highly oriented pyrolytic graphite in sulfuric acid solution. *J Electrochem Soc* 2007;154:B1017–23.
- [24] Zhang W, Xi J, Li Z, Zhou H, Liu L, Wu Z, et al. Electrochemical activation of graphite felt electrode for  $\text{VO}^{2+}/\text{VO}_2^+$  redox couple application. *Electrochim Acta* 2013;89:429–35.
- [25] Kaneko H, Nozaki K, Wada Y, Aoki T, Negishi A, Kamimoto M. Vanadium redox reactions and carbon electrodes for vanadium redox flow battery. *Electrochim Acta* 1991;36:1191–6.
- [26] Madić C, Begun GM, Hahn RL, Launay JP, Thiessen WE. Dimerization of aquadioxovanadium(V) ion in concentrated perchloric and sulfuric acid media. *Inorg Chem* 1984;23:469–76.
- [27] Gençten M, Dönmez KB, Şahin Y, Pekmez K, Suvacı E. Voltammetric and electrochemical impedimetric behavior of silica-based gel electrolyte for valve-regulated lead-acid battery. *J Solid State Electrochem* 2014;18:2569–79.
- [28] Gao C, Wang N, Peng S, Liu S, Lei Y, Liang X, et al. Influence of Fenton's reagent treatment on electrochemical properties of graphite felt for all vanadium redox flow battery. *Electrochim Acta* 2013;88:193–202.
- [29] Yue L, Li W, Sun F, Zhao L, Xing L. Highly hydroxylated carbon fibres as electrode materials of all-vanadium redox flow battery. *Carbon* 2010;48:3079–90.