

NH₄H₂PO₄ Solution Treated Graphite Felt as the Positive Electrode for All-vanadium Redox Flow Battery

Bingxue Hou*, Xumei Cui

College of Materials Engineering, Panzhuhua University, Panzhuhua 617000, China
 416517865@qq.com

This paper treats the polyacrylonitrile (PAN)-based graphite felt (GF) with hydrothermal NH₄H₂PO₄ solution and adopts the treated GF as the positive electrode of all-vanadium redox flow battery (VRFB). Specifically, the GF was treated in a teflon-lined stainless-steel autoclave with 1.6M NH₄H₂PO₄ solution for 4h at 60°C. Then, structure, composition and electrochemical properties of the GF were characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). The test results indicate that the NH₄H₂PO₄ was successfully absorbed on the surface of GF after the treatment; the treated GF had better electrochemical activity in V(IV)/V(V) redox reaction (at 10mVs⁻¹) than the untreated GF; the oxidation and reduction peak current densities of the treated GF increased by 19.5% and 57.1%, respectively. According to the CV measurement at various scan rates, the treated GF enjoyed better mass transfer properties of V(V) ions than the untreated GF. These results demonstrate that NH₄H₂PO₄ absorbed on the carbon surface can enhance the electrochemical activity of the GF in the VRFB system.

1. Introduction

Proposed by Skyllas-Kazacos et al. in 1985, the all-vanadium redox flow battery (VFRB) is an environmental-friendly battery, featuring low cost, long lifecycle, flexible design, fast response and deep discharge (Sum et al., 1985; Sum et al., 1985; Skyllaskazacos et al., 1986). In the VFRB, the electrochemical reactions of vanadium ions occur on the electrode surface with H₂SO₄ solution as the supporting electrolyte (Chakrabarti et al., 2007; Zhong et al., 1992). Over the years, much research has been done on electrode made of carbon materials, including carbon paper, graphite felt, carbon felt, carbon nanotube, graphene, and so on (Blasi et al., 2014; Zhong et al., 1993; Li et al., 2015; González et al., 2011; Han et al., 2011; Jeong et al., 2015; Yue et al., 2010;). Among all the carbon electrode materials, polyacrylonitrile (PAN)-based graphite felt (GF) stands out as the most investigated and commonly used electrode material in VFRB, thanks to its reasonable cost, wide potential range, large surface area, and stability in high acidic solutions (Zhong et al., 1993; Kaneko et al., 1991;). Nevertheless, the GF electrode may drag down the voltage efficiency and power density of the VFRB, due to its poor electrochemical activity and surface hydrophobicity (Shao et al., 2010, Zhu et al., 2008). What is worse, the battery performance is heavily influenced by the slower dynamic reaction at the positive redox couple than that at the negative electrode. The disparity of the reaction speed is attributable to the coordination structure rearrangement of vanadium ions (Flox et al., 2012).

In view of the downsides of the PAN-based GF, it is imperative to develop an effective method to modify the positive electrode and improve its electrochemical properties. The existing modification methods mainly fall into the categories of metal electrodeposition (Sun et al., 1991), oxidation (Sun et al., 1992; Sun et al., 1992; Chen et al., 2014), nitrogenization (Wu et al., 2012; Wang et al., 2012), and utilization of carbon nanotube/graphene (Ejigu et al., 2015; Moghim et al., 2017; González et al., 2017). According to Cong Ding et al. (Ding et al., 2015), some phosphate salts, e.g. the NH₄H₂PO₄, can significantly improve the reversibility and activity of redox reaction. Therefore, this paper proposes to treat the GF electrodes of the VFRB with hydrothermal NH₄H₂PO₄ solution.

2. Experiment

2.1 Sample preparation

The commercial PAN-based GF (SGL Carbon) was used as the electrode material. First, the GF was cleaned in ethanol water (70%) under ultrasonication for 0.5h to remove impurities in the fibres, washed with distilled water and dried at 60°C for 24h. Some of the purified GF was assigned to the control group as the untreated sample, and some was immersed in a teflon-lined stainless steel autoclave with 1.6M $\text{NH}_4\text{H}_2\text{PO}_4$ solution at 60°C for 4h. Then, the treated samples were taken out, washed thoroughly with distilled water, and dried at 60°C for 24h.

2.2 Morphology characterization

The surface morphology of the GFs was characterized with JSM-7500F (JEOL) scanning electron microscopy (SEM), and the surface chemistry of the GF was measured by Nicolet 6700 X-ray photoelectron spectroscopy (XPS) (Thermo Scientific).

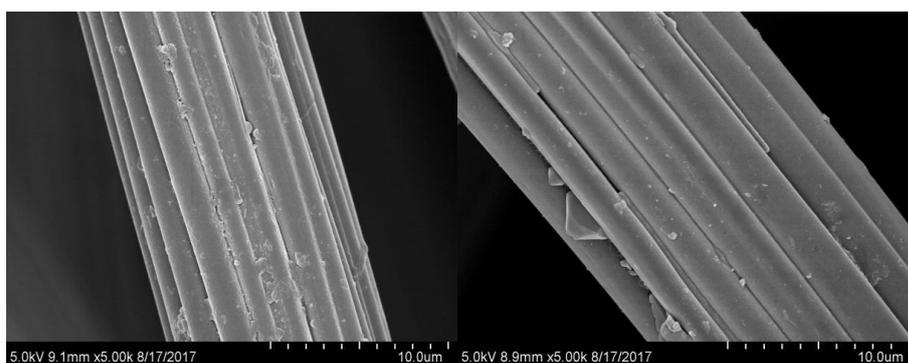
2.3 Electrochemical measurement

In the potential range of 0~1.6V, a cyclic voltammetry (CV) test was performed on CHI660 electrochemical workstation (Shanghai Chenhua) at various scan rates under room temperature. A three-electrode battery was employed with Pt electrode as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and a GF (1cm²) as the working electrode. The electrolyte was a mixture of 0.1M VOSO_4 solution and 3M H_2SO_4 solution. Besides, an electrochemical impedance spectroscopy (EIS) test was also performed on the CHI660 electrochemical workstation. The impedance spectra were obtained by applying an alternating voltage of 5mV over the frequency ranging from 10^{-2} to 10^{-5} Hz.

3. Results and discussion

3.1 Morphology characterization

Figure 1 shows the surface morphology of the GF. It can be clearly seen that there is no visible change of the surface morphology for untreated GF and treated GF. For untreated GF (Figure 1a), even after purification procedure, the surface has more impurities which were introduced in the process of GF production. After being treated with the treatment with hydrothermal $\text{NH}_4\text{H}_2\text{PO}_4$ solution, the impurities on the GF surface (Figure 1b) decreased significantly, which greatly enhanced the ability to adsorb vanadium ions and transfer electron. Therefore, the treatment with hydrothermal $\text{NH}_4\text{H}_2\text{PO}_4$ solution can further remove the impurities on the surface of GF.



(a) untreated GF

(b) treated GF

Figure 1: SEM images of GF

3.2 X-ray photoelectron spectroscopy

As can be seen from the XPS spectra of the GF (Figure 2), the O1s, N1s and P2p signals on the treated GF were much stronger than those on the untreated GF. The content changes of elements on the GF surface are listed in Table 1. Whereas the untreated GF had almost nitrogen (1.13%) or phosphorus (0.38%), the content of nitrogen and phosphorus in the treated GF increased to 4.28% and 2.54%, respectively. Moreover, the

treated GF also had a slightly higher oxygen content than the untreated GF. The results indicate that the $\text{NH}_4\text{H}_2\text{PO}_4$ had been adsorbed by the GF.

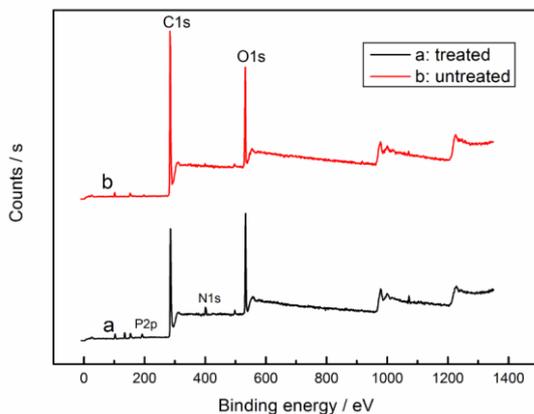


Figure 2: XPS spectra of the GF

Table 1: Content change of elements on the surface of GF from XPS.

Sample	C1s	O1s	N1s	P2p
Untreated GF (%)	79.63	18.86	1.13	0.38
Treated GF (%)	69.69	23.49	4.28	2.54

3.3 Electrochemical performance

The CV behaviours of GF for positive electrode were measured at the scan rate of 10mVs^{-1} (Figure 3). It can be seen that the samples exhibited an anodic peak associated with the oxidation of V(IV) to V(V); the corresponding reduction peaks appeared at 1.0~1.1 V (GF) and 0.65~0.75 V (SCE), respectively. For the convenience of comparison, the electrochemical parameters were set to the values listed in Table 2. The treated GF had a 19.5% higher oxidation peak current density and a 57.1% higher reduction peak current density than the untreated GF; the ratio of anodic peak current to cathodic peak current (I_{pa}/I_{pc}) for V(IV)/V(V) redox reaction is closer to 1, an evidence to the improved redox kinetics. The potential gaps between oxidization and reduction peaks (ΔE_p) of the treated GF was much lower than that of the untreated GF, which implies that the treated GF had better electrochemical reversibility.

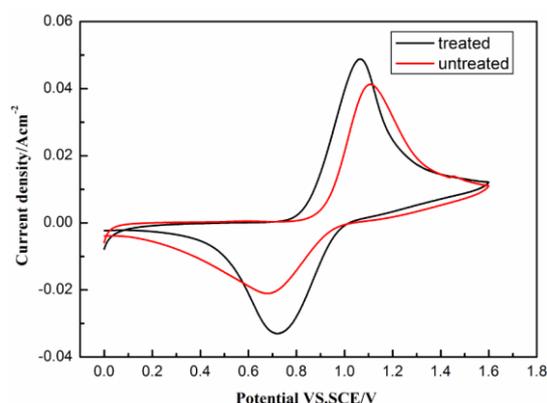


Figure 3: Cyclic voltammograms curves of the GF at a scan rate of 10mVs^{-1} .

Table 2: Content change of elements on the surface of GF from XPS.

Sample	Anodic peak I_{pa} [A]	Cathodic peak I_{pc} [A]	ΔE_p [V]	I_{pa}/I_{pc}
Untreated GF	0.041	0.021	0.437	1.95
Treated GF	0.049	0.033	0.343	1.48

To further explore the reaction reversibility, the CV curves of GF were obtained at different scan rates. The treated GF had better symmetry and higher peak current than the untreated GF at the same scan rate,

revealing that the polarization was decreased because of the enhanced electrochemical activity. In addition, the oxidation and reduction peak potentials varied gradually with the scanning rate, which implies the redox reaction of V(IV)/V(V) couple on graphite electrode is the typical characteristics of a quasi-reversible one-electron process (Sun et al., 1992). For the active species on the GF electrodes, the mass transfer properties were estimated by plotting the oxidation peak current as a function of the square root of scan rates (Figure 5). As shown in Figure 5, the peak current increased linearly with the growth of scan rate. Since the slope of the curve is positively correlated with the diffusion performance of active species (Liu et al., 2014; Shen et al., 2015), it is concluded that the treated GF enjoyed better mass transfer ability for V(IV)/V(V) ions than the untreated GF.

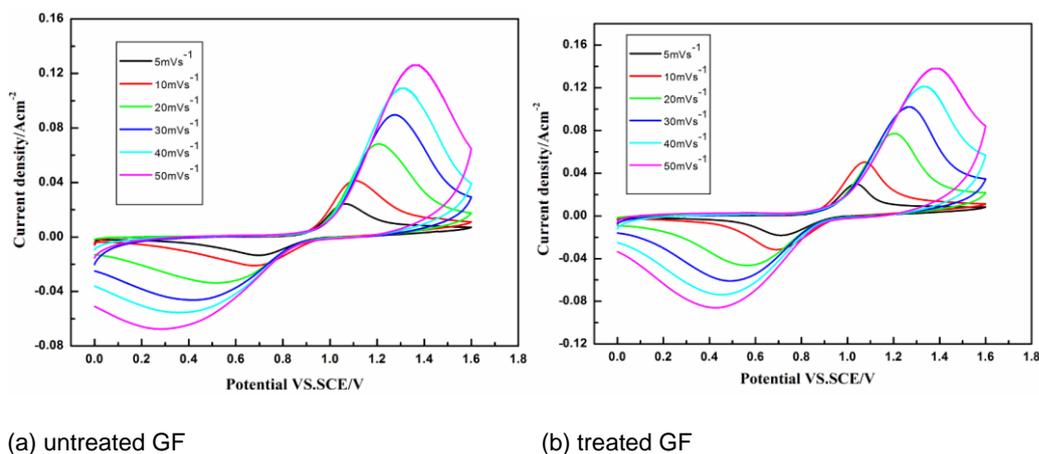


Figure 4: CV curves of the GF at different scan rates

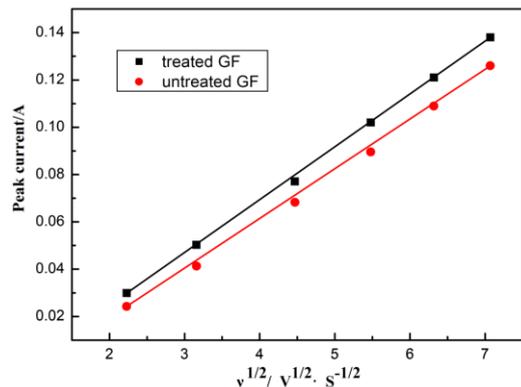


Figure 5: Plots of the anodic peak current vs. square root of scan rates for GF

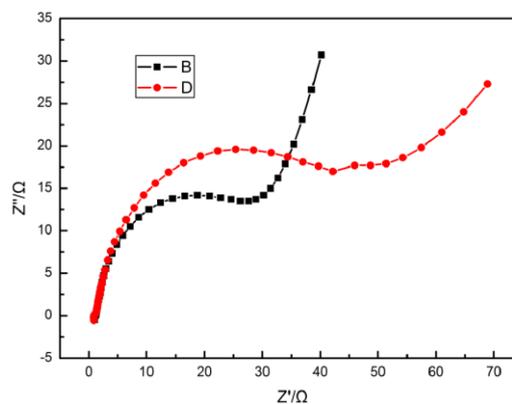


Figure 6: Nyquist plots of untreated GF (D) and treated GF (B)

To deepen the understanding of the effect of the treated GF on the electrode reaction, the author conducted an EIS test in the 0.1 M $\text{VOSO}_4 + 3\text{M H}_2\text{SO}_4$ solution at open-circuit potential, and drawn the Nyquist plots of the GF electrodes (Figure 6). It is observed that all the plots carried a similar pattern, consisting of a semicircle in the high frequency region (charge transfer process) and a straight line part in the low frequency region (diffusion process); the radius was equal to the charge transfer resistance (i.e. the smaller the radius, the faster the reaction) (Hsieh et al., 2010; Wu et al., 2014). The results confirm that the electrochemical process was mix-controlled by charge transfer and diffusion processes. The untreated GF electrode had a larger semi-arc radius than the treated GF, and thus a larger charge transfer resistance. Similarly, the treated GF had a smaller charge transfer resistance, and thus a faster reaction speed. It is obvious that the $\text{NH}_4\text{H}_2\text{PO}_4$ adsorbed on the GF electrode surface promoted the V(IV)/V(V) redox reaction, and substantially reduced the charge transfer resistance. The conclusion is in good agreement with the CV results (Figure 6).

4. Conclusions

After being treated with hydrothermal $\text{NH}_4\text{H}_2\text{PO}_4$ solution, the GF positive electrode exhibited a better electrochemical performance in the V(IV)/V(V) redox reaction. The treated GF had a 19.5% higher oxidation peak current density and a 57.1% higher reduction peak current density than the untreated GF. The ΔE_p (0.343V) of the treated GF was 21.5% lower than that of the untreated GF, while the charge transfer resistance of the treated GF was smaller than that of the untreated GF. These results demonstrate that $\text{NH}_4\text{H}_2\text{PO}_4$ absorbed on the carbon surface can enhance the electrochemical activity of the GF in the VRFB system.

Acknowledgments

This research was financially supported by Science and Technology Plan Projects of Panzhihua (No. 2014CY-G-28), Titanium and titanium alloy innovation team (No. 2013TX8) and Sichuan Provincial Department of education project (No.16ZA0410).

References

- Blasi A.D., Briguglio N., Blasi O.D., Antonucci V., 2014, Charge–discharge performance of carbon fiber-based electrodes in single cell and short stack for vanadium redox flow battery, *Applied Energy*, 152(2), 114-122, DOI: 10.1016/j.apenergy.2014.03.043
- Chakrabarti M.H., Dryfe R.A.W., Roberts E.P.L., 2007, Evaluation of electrolytes for redox flow battery applications, *Electrochimica Acta*, 52(5), 2189-2195, DOI: 10.1016/j.electacta.2006.08.052
- Chen J.Z., Liao W.Y., Hsieh W.Y., Hsu C.C., Chen Y.S., 2014, All-vanadium redox flow batteries with graphite felt electrodes treated by atmospheric pressure plasma jets, *Journal of Power Sources*, 274, 894-898, DOI: 10.1016/j.jpowsour.2014.10.097
- Ding C., Ni X., Li X., Xi X., Han X., Bao X., Zhang H., 2015, Effects of phosphate additives on the stability of positive electrolytes for vanadium flow batteries, *Electrochimica Acta*, 164(12), 307-314, DOI: 10.1016/j.electacta.2015.02.187
- Ejigu A., Edwards M., Walsh D.A., 2015, Synergistic catalyst–support interactions in a graphene– Mn_3O_4 electrocatalyst for vanadium redox flow batteries, *ACS Catalysis*, 5, 7122–7130, DOI: 10.1021/acscatal.5b01973
- Flox C., Rubio-Garcia J., Nafria R., Zamani R., Skoumal M., Andreu T., Arbiol J., Cabot A., Morante J.R., 2012, Active nano-CuPt 3 electrocatalyst supported on graphene for enhancing reactions at the cathode in all-vanadium redox flow batteries, *Carbon*, 50(6), 2372-2374, DOI: 10.1016/j.carbon.2012.01.060
- González Z., Flox C., Blanco C., Granda M., Morante J.R., Menéndez R., Santamaría R., 2017, Outstanding electrochemical performance of a graphene-modified graphite felt for vanadium redox flow battery application, *Journal of Power Sources*, 338, 155-162, DOI: 10.1016/j.jpowsour.2016.10.069
- González Z., Sánchez A., Blanco C., Granda M., Menéndez R., Santamaría R., 2011, Enhanced performance of a Bi-modified graphite felt as the positive electrode of a vanadium redox flow battery, *Electrochemistry Communications*, 13(12), 1379-1382, DOI: 10.1016/j.elecom.2011.08.017
- Han P., Yue Y., Liu Z., Xu W., Zhang L., Xu H., Dong S., Cui G., 2011, Graphene oxide nanosheets/multi-walled carbon nanotubes hybrid as an excellent electrocatalytic material towards $\text{VO}_2^+/\text{VO}_2^{2+}$ redox couples for vanadium redox flow batteries, *Energy & Environmental Science*, 11(4), 1379-1382, DOI: 10.1039/C1EE01776D
- Hsieh C.T., Teng H., Chen W.Y., Cheng Y.S., 2010, Synthesis, characterization, and electrochemical capacitance of amino-functionalized carbon nanotube/carbon paper electrodes, *Carbon*, 48(15), 4219-4229, DOI: 10.1016/j.carbon.2010.07.021
- Jeong S., An S., Jeong J., Lee J., Kwon Y., 2015, Effect of mesocellular carbon foam electrode material on performance of vanadium redox flow battery, *Journal of Power Sources*, 278, 245-254, DOI: 10.1016/j.jpowsour.2014.12.074
- Kaneko H., Nozaki K., Wada Y., Aoki T., Negishi A., Kamimoto M., 1991, Vanadium redox reactions and carbon electrodes for vanadium redox flow battery, *Electrochimica Acta*, 36(7), 1191-1196, DOI: 10.1016/0013-4686(91)85108-J
- Li W., Zhang Z., Tang Y., Bian Ha., Ng T.W., Zhang W., Lee C., 2015, Graphene-nanowall-decorated carbon felt with excellent electrochemical activity toward $\text{VO}_2^+/\text{VO}_2^{2+}$ couple for all vanadium redox flow battery, *Advanced Science*, 3(4), 1500276, DOI: 10.1002/advs.201500276
- Liu J., Liu S., He Z., Han H., Chen Y., 2014, Effects of organic additives with oxygen- and nitrogen-containing functional groups on the negative electrolyte of vanadium redox flow battery, *Electrochimica Acta*, 130(4), 314-321, DOI: 10.1016/j.electacta.2014.02.116

- Moghim M.H., Eqra R., Babaiee M., Zarei-Jelyani M., Loghavi M.M., 2017, Role of reduced graphene oxide as nano-electrocatalyst in carbon felt electrode of vanadium redox flow battery, *Journal of Electroanalytical Chemistry*, 789, 67-75, DOI: 10.1016/j.jelechem.2017.02.031
- Shao Y., Wang X., Engelhard M., Wang C., Sheng D., Liu J., Yang Z., Lin Y., 2010, Nitrogen-doped mesoporous carbon for energy storage in vanadium redox flow batteries, *Journal of Power Sources*, 195(13), 4375-4379, DOI: 10.1016/j.jpowsour.2010.01.015
- Shen J., Liu S., He Z., Shi L., 2015, Influence of antimony ions in negative electrolyte on the electrochemical performance of vanadium redox flow batteries, *Electrochimica Acta*, 151, 297-305, DOI: 10.1016/j.electacta.2014.11.060
- Skyllaskazacos M., Rychcik M., Robins R.G., Fane A.G., Green M.A., 1986, New all-vanadium redox flow cell, *Journal of the Electrochemical Society*, 133(5), 1057, DOI: 10.1149/1.2108706
- Sum E., Rychcik M., Skyllas-Kazacos M., 1985, Investigation of the V(V)/V(IV) system for use in the positive half-cell of a redox battery, *Journal of Power Sources*, 16(2), 85-95, DOI: 10.1016/0378-7753(85)80082-3
- Sum E., Skyllas-Kazacos M., 1985, A study of the V(II)/V(III) redox couple for redox flow cell applications, *Journal of Power Sources*, 15(2), 179-190, DOI: 10.1016/0378-7753(85)80071-9
- Sun B., Skyllas-Kazacos M., 1991, Chemical modification and electrochemical behaviour of graphite fibre in acidic vanadium solution, *Electrochimica Acta*, 36(3-4), 13-517, DOI: 10.1016/0013-4686(91)85135-T
- Sun B., Skyllas-Kazacos M., 1992, ChemInform Abstract: modification of graphite electrode materials for vanadium redox flow battery application, Part 1. Thermal Treatment, *Cheminform*, 23(34), 1253-1260, DOI: 10.1016/0013-4686(92)85064-R
- Sun B., Skyllas-Kazacos M., 1992, Modification of graphite electrode materials for vanadium redox flow battery application—I. Thermal treatment, *Electrochimica Acta*, 37(34), 1253-1260, DOI: 10.1016/0013-4686(92)85064-R
- Wang S., Zhao X., Cochell T., Manthiram A., 2012, Nitrogen-doped carbon nanotube/graphite felts as advanced electrode materials for vanadium redox flow batteries, *Journal of Physical Chemistry Letters*, 3(16), 2164-2167, DOI: 10.1021/jz3008744
- Wu T., Huang K., Liu S., Zhuang S., Fang D., Li S., Lu D., Su A., 2012, Hydrothermal ammoniated treatment of PAN-graphite felt for vanadium redox flow battery, *Journal of Solid State Electrochemistry*, 16(2), 579-585, DOI: 10.1007/s10008-011-1383-y
- Wu X., Xu H., Xu P., Shen Y., Lu L., Shi J., Fu J., Zhao H., 2014, Microwave-treated graphite felt as the positive electrode for all-vanadium redox flow battery, *Journal of Power Sources*, 263(4), 104-109, DOI: 10.1016/j.jpowsour.2014.04.035
- Yue L., Li W., Sun F., Zhao L., Xing L., 2010, Highly hydroxylated carbon fibres as electrode materials of all-vanadium redox flow battery, *Carbon*, 48(11), 3079-3090, DOI: 10.1016/j.carbon.2010.04.044
- Zhong S., Padeste C., Kazacos M., Skyllas-Kazacos M., 1993, Comparison of the physical, chemical and electrochemical properties of rayon- and polyacrylonitrile-based graphite felt electrodes, *Journal of Power Sources*, 45(1), 29-41, DOI: 10.1016/0378-7753(93)80006-B
- Zhong S., Skyllas-Kazacos M., 1992, Electrochemical behaviour of vanadium(V)/vanadium(IV) redox couple at graphite electrodes, *Journal of Power Sources*, 39(1), 1-9, DOI: 10.1016/0378-7753(92)85001-Q
- Zhu H., Zhang Y., Yue L., Li W., Li G., Shu D., Chen H., 2008, Graphite-carbon nanotube composite electrodes for all vanadium redox flow battery, *Journal of Power Sources*, 184(2), 637-640, DOI: 10.1016/j.jpowsour.2008.04.016