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INFLUENCE OF SIO_2 NANOPARTICLES ON THE CHARACTERISTICS OF A POLYVINYL ALCOHOL-BASED PROTON EXCHANGE COMPOSITE MEMBRANE

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This paper presents a study of nanocomposite membranes based on cross-linked polyvinyl alcohol with silica nanoparticles, fabricated by solution casting, for application in vanadium redox batteries (VRFBs). The structure of the membranes was studied by Fourier transform infrared spectroscopy (FT-IR). It was found that the nanoparticles were successfully integrated into the matrix of the proton exchange membrane to improve its performance. The synthesis of silica nanoparticles by in situ sol-gel method in polymer solution showed better performance compared to the addition of prepared nanoparticles. The membrane properties such as mechanical properties, water absorption, ion exchange material (IEM), proton conductivity and permeability to vanadium ions were investigated. The nanocomposite membranes showed higher water absorption, IEM and lower permeability for vanadium ions compared to Nafion117 membrane. The test results of single cell VRFB with nanocomposite membranes showed higher Coulomb yield (CE) and efficiency (EE) up to 81.51% compared to Nafion117. The self-discharge rate of VRFBs with nanocomposite membranes was lower than that of Nafion117. After 50 test cycles, the nanocomposite membrane showed stable battery performance. The results indicate that nanocomposite membranes are a promising and affordable alternative material for Nafion117 in VRFBs.

Keywords: *Proton exchange membrane; Nanocomposite membranes; Polyvinyl alcohol-based separation membranes; Nafion117; Vanadium redox flow batteries; Tetroethoxysilane; Alkylbenzosulfonic acid*
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1. INTRODUCTION

Vanadium redox flow batteries (VRFBs) have attracted much attention in recent decades due to their outstanding advantages such as low cost, high efficiency, good cyclic stability and promising applications in large-scale energy storage. In VRFBs, the proton exchange membrane (PEM) is an important separator between the catholyte and anolyte, which prevents the mixing of electrolytes while allowing the migration of conductive H^+ and SO_4^{2-} ions to complete the electrical circuit. An ideal PEM should have high ionic conductivity, low permeability to vanadium, high mechanical strength and good chemical stability [1]. For real commercialization of VRFB, the cost of its separator is crucial. Although many high-performance PEMs can be prepared from specially designed polymers and fillers, the cost associated with the complete synthesis process can be very high. In addition, these syntheses cannot be easily scaled up. The most widely used Nafion membranes, typical perfluorinated sulfonic acid polymeric materials developed by DuPont, are recognized as a reference material for VRFBs due to their high proton conductivity and excellent chemical stability. However, problems with the high permeability to vanadium in Nafion membranes, as well as their low ion selectivity and high cost, still limit their widespread application in VRFBs [2]. Sulfinated polymers have attracted attention because of their good proton conductivity over a wide temperature range and low fabrication cost [3]. Modification or synthesis conditions due to the use of strong sulfating agents lead to partial degradation of the polymer chain and cause undesirable change in the polymer by rearrangement of intermediate functional units of sulfo groups [4]. As another disadvantage, there are reports in which the sulfonic group undergoes substitution by electrophilic aromatic proton substitution mechanicm to reduce the hydrolytic stability of the membrane [5]. To address these drawbacks, polymerization of sulfated aromatic monomers [6] is underway, but the use of expensive catalysts limits its large-scale production. Meanwhile, the preparation of commercial anion exchange membrane involves chloromethylation using chloromethyl methyl ether which is considered hazardous to the environment, followed by amination of polymers [7].

To eliminate such operations such as sulfation/amination, an alternative approach is to provide the polymer matrix with inorganic materials to obtain inorganic-organic composite ion exchange membranes that will have the properties and characteristic features of inorganic and organic compounds [8]. The inherent hydrophilicity of polyvinyl alcohol (PVA), abundant reactive hydroxyl groups and low cost are reasons for its selection as a typical host matrix [9]. Among the numerous inorganic materials, silica, including porous silicon, which has demonstrated significant potential for solar energy applications [10], is the most commonly used inorganic filler used in PVA matrix to improve the mechanical strength, thermal stability, water retention capacity and proton conductivity of the membrane [11]. Incorporation of silica nanoparticles into the PVA membrane using a solution-gel in situ (sol-gel) process is a novel approach compared to direct physical mixing [12]. Silicon dioxide nanoparticles in the composite is dominated by certain interconnected conductive channels due to the uniform distribution of nanoparticles [13]. The compatibility of organic and inorganic phases is

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determined by multiple covalent bonds, hydrogen bonds and electrostatic interactions [14]. Enhancement of proton conductivity in PVA/SiO_2 composite membranes is achieved by various strategies, of which the most common practices include (a) incorporation of functionalized silica, (b) functionalization of PVA, and (c) blending of PVA/SiO_2 with charged polymers/nanomaterials [15-16]. A group of scientists created based on the above methods used to fabricate a PVA/SiO_2 composite separator with high proton conductivity for energy devices [17]. Hybrid membranes have been developed by dispersing sulfated nanosilica in a cross-linked PVA matrix with sulfated tetraethoxysilane (TEOS) [18]. The PVA and chitosan membrane composite with silica gel functionalized with poly (2-acrylamido-2-methyl-1-propanesulfonic acid) showed good thermal and oxidative stability [19]. Controlling the level of functionalization and crosslinking plays a key role, as excessive functional groups can impair the mechanical stability and insufficient crosslinking negatively affects the membrane stability.

The aim of the present study is to investigate the effect of different types of silica nanoparticles on the properties of proton exchange membranes. This paper presents the synthesis of PVA/SiO_2 composite membrane by mixing silica nanoparticles with PVA. Two membranes were fabricated in which SiO_2 was filled with SiO_2 by sentinel sol gel method in polymer solution and prepared with mechanical solution blending of prepared SiO_2 nanopowder. The SiO_2 and PVA matrix functioned as a barrier for vanadium ions, formed a well-defined conductive structure to transfer charge balancing hydrated protons during vanadium flow battery operation.

2. EXPERIMENTAL

For the experiments we used standard PVA grade “h” with viscosity 18 mPa×s and degree of hydrolysis 89%, (average M=85000-146000 g/mol), tetroethoxysilane (TEOS) and similar alkylbenzosulfonic acid (ABSA), succinic acid “hh”, hydrochloric acid grade “hh” and on Sigma-Aldrich. The prepared silica nanopowders were obtained from the authors [20], pre-milled with a Retsch PM-400 nanomill (Germany) to mechanically activate the powdered material. Deionized water with a resistivity of 10 MΩ was used. To compare the characteristics of the obtained membranes we used a commercial sample of Nafion117 membrane from DuPont Co.

To prepare the first membrane sample, an aqueous solution of PVA with concentrations of 2.5, 5 and 10 wt.% was prepared by dissolving PVA in deionized water at 80°C and stirring constantly for 6 hours. The solution was cooled to room temperature before adding succinic acid at a molar ratio of PVA:JA of 1:0.25. The solution was stirred at 70°C for 4 hours. After that, a solution of H_2O, HCl and TEOS taken in the molar ratio of 5:0, 1:1 was added. Stirring was continued for another 2 hours, then the solution was poured into Plexiglas and then heated at 40°C for 24 hours to induce cross-linking reaction. The resulting membrane was separated and then soaked in 0.5 M alkylbenzosulfonic acid solution for 1 hour. The membrane was heated at 40°C for 2 hours to delineate the crosslinking reaction. Before molding, the mixture was ultrasonicated for 30 min to avoid aggregation. The resulting composite membranes were labelled as 1-PVA/SiO_2.

For the preparation of the second membrane sample, the synthesis sequence was carried out in the same way, only after complete dissolution of the polymer, mechanically activated silica nanopowder was added. The rest of the synthesis steps were continued accordingly. The obtained composite membranes were denoted as 2-PVA/SiO_2.

FT-IR spectra of the membranes were measured on a Nicolet 6700 spectrometer instrument in the range of 4000-600 cm^{-1}. The samples were dried at 50°C for 2 h before measurement. The mechanical properties of the blended membranes were measured using a Shimadzu AGS-X. rupture machine at room temperature. The samples were tested at an elongation rate of 5.0 mm/min.

The membranes were dried at 80°C in vacuum for 24 h and the dry weight of the samples was weighed. The membranes were then immersed in deionized water for 24 h at room temperature. After wiping off the water adhering to the surface of the membranes, the mass and dimensions of the wet membranes were measured. The water absorption and swelling coefficient were determined using the following equations:

$$Water\ uptake = \frac{W_{Wet}-W_{dry}}{W_{dry}} \times 100\%,$$

where W_{wet} and W_{dry} are the masses of membranes in wet and dry states, respectively.

$$\text{swelling ratio} = \frac{L_{Wet}-L_{dry}}{L_{dry}} \times 100\%,$$

where L_{wet} and L_{dry} are the size of membranes in wet and dry states, respectively.

Ion exchange capacity of membranes (IEM) was determined by titration method. Dry membranes were immersed in NaCl solution with a concentration of 1 mol/L for 24 hours. This solution was titrated with 0.01 mol l-1NaOH using phenol-phthalein as an indicator. The IEM of the samples was calculated according to the following equation:

$$\text{IEM}=\frac{V(NaOH)\times C(NaOH)}{W_{dry}}.$$

Where V (NaOH) is the volume of NaOH solution consumed, C(NaOH) is the concentration of NaOH solution, and W dry is the weight of dry membrane.

The area resistance of the membranes was measured by the method described in the literature [21]. The measurement was performed using a two-chamber device consisting of two cells separated by a membrane. Both compartments were filled with 1 M H_2SO_4. The effective area of the membrane was 0.500 cm^2. The electrical resistivity was measured by electrochemical impedance spectroscopy (EIS) (CORTEST 350CS, China) in the frequency range of 100 kHz to 100 MHz. The resistance value related to membrane conductivity was determined from the high-frequency intersection of the impedance with the real axis. The area impedance R was calculated using the following expressions:

$$R=(r_1-r_2)S$$

where r_1 and r_2 are electrical resistances of the cell with and without membrane, respectively. Proton conductivity was calculated from the equation:

$$\varrho=L/R$$

where L and R are the thickness and resistance area of the membrane, respectively.

To measure the permeability of vanadium ions, the membranes were exposed to a solution of 1.5 M $VOSO_4$ and 3 M H_2SO_4 (left cell reservoir) and a solution of 1.5 M $MgSO_4$ and 3 M H_2SO_4 (right cell reservoir). $MgSO_4$ was used to equalize ionic strength and reduce the effect of osmotic pressure. The effective membrane area was 0.5 cm^2. Samples from the left cell reservoir were taken at regular intervals and analyzed for vanadium ion concentration using a UV spectrometer (UV-2550, SHIMADZU). Vanadium ion permeability was calculated from the following equation:

$$V_R = \frac{dC_R(t)}{dt} = A_\tau^P[C_L - C_R(t)]$$

where P – is the permeability to vanadium ions, C_L is the concentration of vanadium ions in the left reservoir, and $C_R(t)$ is the concentration of vanadium ions in the right cell reservoir as a function of time. A_τ^p — membrane area, V_R – volume of the cell reservoir. Usually, the change in the concentration of vanadium ions in the left cell reservoir can always be insignificant.

To test the resulting membranes, a single VRB cell was assembled by placing a membrane between two parts of graphite plate electrodes with an effective reaction area of 50 mm^2. The material of the current collector was a graphite plate. The initial negative and positive electrolytes were solutions of 1.5 M V^{3+} in 3.0 M H_2SO_4 and 1.5 and VO^{2+} in 3.0 M H_2SO_4, respectively. The volume of electrolyte on each side of the cell was 100 ml. Both positive and negative electrolytes were cycled into the respective half-cell at a rate of 0.5 L/min. A charge-discharge cycle was conducted at CORTEST 350CS, China with a constant current density of 50 mA cm^{-2} at 25°C. The charge and discharge cutoff voltages were set to 1.65 V and 0.8 V, respectively, to avoid corrosion of graphite felts and graphite plates. Coulomb efficiency (CE), voltage efficiency (VE) and energy efficiency (EE) of the cell are calculated using the following equations:

$$CE = \frac{Q_{discharge}}{Q_{charge}} \times 100\% = \frac{I_{charge}t_{discharge}}{I_{charge}t_{charge}} \times 100\% = \frac{t_{discharge}}{t_{charge}} \times 100\%$$

$$VE = \frac{V_{discharge}}{V_{charge}} \times 100\%$$

$$EE = CE \times VE$$

3. RESULTS AND DISCUSSION

Composite membranes containing silicon dioxide nanoparticles are obtained. During the manufacture of these membranes, 2.5% silica nanoparticles were added to the composition based on the weight of the polymer.

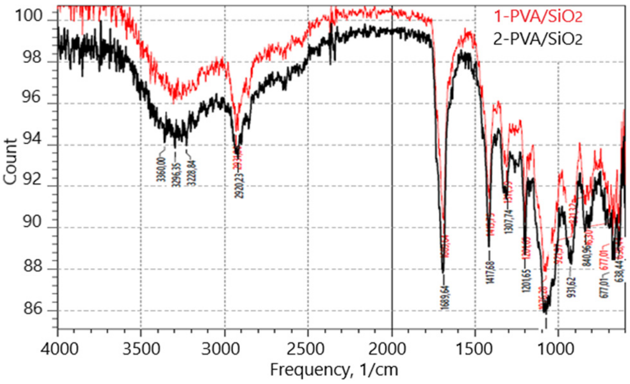

Figure 1. FTIR-ATR spectra of 1-PVA/SiO_2 and 2-PVA/SiO_2 nanocomposite membranes

PVA crosslinking is visible from FT-ATR membrane spectra (Fig. 1). Characteristic peaks of PVA and SiO_2, i.e. ~ 3360 (OH draw), ~ 1450 (OH bend) and ~ 1080 cm^{-1} (C-OH draw) [22] and symmetrical Si-O-Si stretch band at ~ 840 cm^{-1} and asymmetrical Si-O-Si stretch at 1076 – 1201 cm^{-1} were positive for both membranes [23]. On close inspection of the spectra, instead of a broad peak for OH, there is a small protrusion with a certain amount of tensile noise signal, indicating effective thermal crosslinking of the membrane. The spectra also showed characteristic C-H, C = O and C = O bands at 2920, 1049 and 1076 cm^{-1}, respectively. In addition, two characteristic peaks at 1007 and 1034 cm^{-1} were assigned to the bands containing SO_3H- groups, respectively [24].

The water absorption coefficient, the swelling coefficient of the IEM are important parameters for characterizing the proton exchange membrane. Many important properties of the membrane, such as proton conductivity and water uptake, are related to IEM and directly depend on the content of free sulfonic acid groups in the membrane. It can be seen that the IEM of the membranes decreases with an increase in nanoparticles in the polymer matrix by 10% (Table 1). High water uptake can improve proton conductivity. However, this also leads to poor dimensional stability and high permeability of vanadium. It was to regulate these membrane characteristics that silica nanoparticles were introduced into the PVA polymer matrix. In addition, the formation of a crosslinked network structure due to silica nanoparticles reduces the free volume in mixed membranes for water molecules, which leads to a decrease in water absorption. The swelling ratio reflects dimensional stability, and a lower swelling ratio is necessary to maintain the size stability of the membrane for a long time. The permeability of vanadium ions is a crucial parameter for VRFB, which is the ability to prevent mixing of positive and negative electrolytes with each other. Diffusion of vanadium ions through the membrane will lead to self-discharge of the battery. This study measured the permeability to vanadium ions of nanocomposite membranes. The vanadium ion concentration in the right tank versus time is shown in Figure 2 and the calculated vanadium permeability coefficients are shown in Table 1.

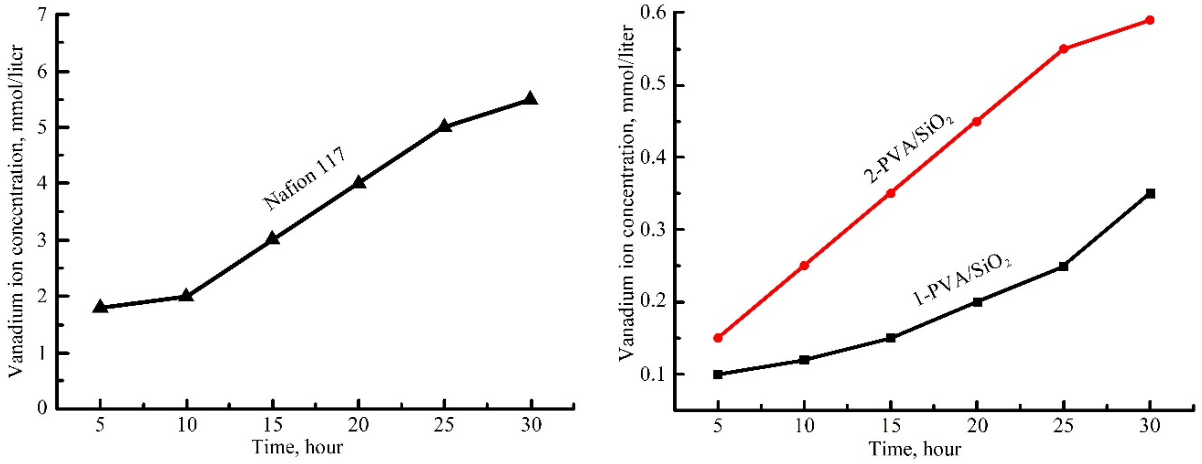

Figure 2. Concentration of vanadium ions in the right cell reservoir by membrane Nafion117 and composite membranes 1-PVA/SiO_2 and 2-PVA/SiO_2

Table 1. Basic properties of nanocomposite membranes and Nafion117 membrane

No.	Membrane type	IEM (mmol/liter)	Swelling ratio (%)	Water uptake (%)	Vanadium ion permeability coefficient (10^{-8} cm^2 s^{-1})	Tensile strength, MPa	Relative lengthening at rupture,%
1	1-PVA/SiO_2						
	2,5% SiO_2	1.47	36.7	22	6.1	2.8	78
	5% SiO_2	1.2	29.5	20	5.8	5.6	52
	10% SiO_2	0.83	21	17	4.7	8.3	43
2	2- PVA /SiO_2						
	2,5% SiO_2	1.13	29.3	21,7	3.8	1.8	50
	5% SiO_2	0.93	23.2	19	3.5	6	85
	10% SiO_2	0.86	26	18	3.4	7.5	27
3	Nafion 117	0.92	20	17	54.8	96	168

All nanocomposite membranes have a lower vanadium ion permeability than the Nafion117 membrane. The permeability of the membrane is 1-PVA/SiO_2, 5.8x10^{-8} cm^2s^{-1} compared to the membrane Nafion117 54.8×$10^{-8}cm^2s^{-1}$. It can also be seen that the permeability of the mixed membranes decreases with increasing silica in the nanocomposite. The difference in vanadium ion permeability between nanocomposite membranes and Nafion117 membrane is determined by their microstructure. The microstructure of the Nafion117 membrane consists of two parts: highly hydrophilic sulfone functional groups and highly hydrophobic fluorocarbon main chains. This will result in hydrophobic/hydrophilic microphase separation. Because of the high flexibility of fluorocarbon, clusters of hydrophilic sulfone groups tended to form hydrophilic domains.

Not only protons, but also vanadium ions could penetrate these membrane domains when used in VRFB. Compared to the Nafion117 membrane, the backbone PVA/SiO_2 less hydrophobic, which prevents the aggregation of dispersed sulfone groups into hydrophilic domains. Thus, the water-filled channels in the membrane are PVA/SiO_2 narrow and branched compared to those in the Nafion117 membrane.

Many important properties, such as proton conductivity and swelling, are associated with IEM. IEM directly depends on the content of free sulfonic acid groups in the membrane. From Table 2. it can be seen that the IEM of the composite membranes did not change and did not depend on the content of silica nanoparticles, but they were closer to those of Nafion 117. Typical charge-discharge curves of a single VRFB with composite membranes and Nafion 117 are shown in Fig. 3. The capacity of a single VRB cell using Nafion117 and composite membranes is shown in Table 2.

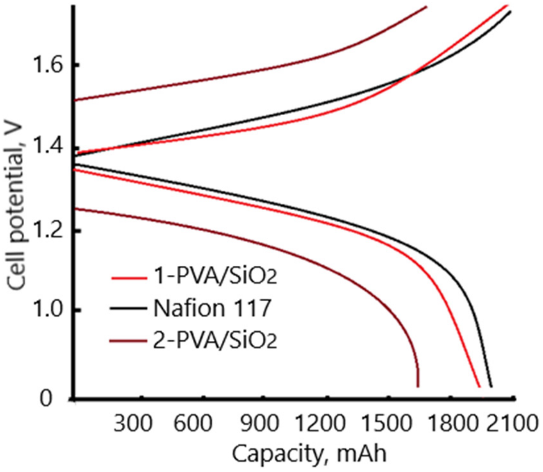

Figure 3. Charge-discharge curves for VRFB with Nafion 117 and membranes 1-PVA/SiO_2 and 2-PVA/SiO_2.

Table 2. Electrochemical properties of nanocomposite and Nafion117 membranes.

№	Membrane type	IEM (mmol g^{-1})	Proton conductivity mS×cm^{-1}	CE(%)	VE(%)	EE(%)
1	1-PVA/SiO_2					
	2,5% SiO_2	0.83	10.9	97.3	70.1	70.36
	5% SiO_2	0.86	12.6	99.5	83.8	81.51
	10% SiO_2	0.82	9.6	94.6	76.3	75.3
2	2- PVA /SiO_2					
	2,5% SiO_2	0.85	10.3	92.3	70.2	70.1
	5% SiO_2	0.82	9.2	91.2	70.8	74.2
	10% SiO_2	0.84	9.8	90.7	73.2	72.8
3	Nafion 117	0.91	12	92.6	83.3	76.8

The discharge test was performed at the same current density of 50 mA cm^{-2} for all membranes. Coulomb efficiency of VRB with all composite membranes showed almost the same efficiency compared to VRB with Nafion117 membrane. In addition, n CE increased from 97.3% to 99.5% by increasing the amount of silica from 2.5% to 5% in the sol-gel 1-PVA/SiO_2 membranes and then decreased to 94.6% in the 10% silica membrane. In 2-PVA/SiO_2 membranes, CE showed values of about 90-92%. This is because the CE of VRFB is determined by the membrane permeability to vanadium ions and ion permeability. All composite membranes have significantly lower permeability than the Nafion117 membrane. In addition, with an increase in silica, the proton conductivity of vanadium ions and the conductivity of vanadium ions decrease. Thus, a balance between ion permeability and vanadium permeability can be achieved by varying the composition of the composite membranes in the VRFB system.

4. CONCLUSIONS

Nanocomposite membranes based on cross-linked polyvinyl alcohol with silicon dioxide nanoparticles were made by solution casting for use in VRFB. The membrane structure was characterized by FT-IR methods. The results showed that the nanocomposites were successfully embedded in the proton-exchange membrane matrix and showed good results. The synthesis of silica nanoparticles by sol gel method in a polymer solution has been established to give the membrane better qualities than the addition of finished nanoparticles in a polymer solution. Membrane properties such as mechanical properties, water absorption, IEM, proton conductivity and vanadium ion permeability were investigated. Compared to

Nafion117 membranes, nanocomposite membranes showed high water absorption, IEM and lower permeability to vanadium ions. In a single cell test, VRFB with nanocomposite membranes showed a higher CE than Nafion117, EE membranes up to 81.51%. The self-discharge rate of VRFB with the nanocomposite membrane was lower than that of the Nafion117 membrane. After 50 test cycles, the mixed membrane showed stable battery performance. Given these results, nanocomposite membrane membranes are expected to be ideal available membranes that can Nafion117 competitive for VRFB applications.

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ВПЛИВ НАНОЧАСТИНОК SIO_2 НА ХАРАКТЕРИСТИКИ ПРОТОНООБМІННОЇ КОМПОЗИТНОЇ МЕМБРАНИ НА ОСНОВІ ПОЛІВІНІЛОВОГО СПИРТУ

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У цій статті представлено дослідження нанокомпозитних мембран на основі зшитого полівінілового спирту з наночастинками кремнезему, виготовлених методом лиття з розчину, для застосування в ванадієвих окисно-відновних батареях (VRFB). Структуру мембран вивчали методом інфрачервоної спектроскопії з перетворенням Фур'є (FT-IR). Було виявлено, що наночастинки були успішно інтегровані в матрицю протонообмінної мембрани для підвищення її продуктивності. Синтез наночастинок кремнезему золь-гель методом in situ в розчині полімеру показав кращу продуктивність порівняно з додаванням готових наночастинок. Були досліджені такі властивості мембрани, як механічні властивості, водопоглинання, іонообмінний матеріал (IEM), протонна провідність і проникність для іонів ванадію. Нанокомпозитні мембрани продемонстрували вищі водопоглинання, IEM і нижчу проникність для іонів ванадію порівняно з мембраною Nafion117. Результати випробувань однокомпонентного VRFB з нанокомпозитними мембранами показали вищий кулонівський вихід (CE) і ефективність (EE) до 81,51% порівняно з Nafion117. Швидкість саморозряду VRFB з нанокомпозитними мембранами була нижчою, ніж у Nafion117. Після 50 циклів тестування нанокомпозитна мембрана показала стабільну роботу акумулятора. Результати показують, що нанокомпозитні мембрани є перспективним і доступним альтернативним матеріалом для Nafion117 у VRFB.

Ключові слова: *протонообмінна мембрана; нанокомпозитні мембрани; роздільові мембрани на основі полівінілового спирту; Нафіон117; ванадієві окисно-відновні батареї; тетроетоксисилан; алкілбензосульфонова кислота*