UDC 621.351 doi: 10.33609/2708-129X.89.02.2023.91-99

FORMATION OF ACTIVE INTERPHASE ON THE IRON PARTICLES IN C/PVDF ELECTROCHEMICAL SYSTEMS

Panteleimonov R.A.[1], Shcherbatiuk I.M.[2], Pershina K.D.[1,2]

[1]V.I.Vernadskyi Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine, Prospect Palladina, 32/34, 03142, Kyiv, Ukraine,
[2]Joint Department of Electrochemical Energy Systems, National Academy of Sciences of Ukraine, Prospect Vernadskoho, 38, 03142, Kyiv, Ukraine
e-mail: radik20031@gmail.com

The possibility of formation of an active interphase on iron particles in C/PVDF has been dictated by the thermochemical reactions of iron and iron oxides in the presence of carbon. The composition with polyvinylidene fluoride (PVDF) changed the redox activity of iron particles and decreased pure iron (Fe^0) amount by 0,24 wt. %. The surface properties of various compositions have been characterized by scanning electron microscopy with the analytical mode for determining the relationship between the microstructure and local thermal reactions on the iron particle surface. A relationship between the surface composition, morphology and electrochemical behavior of the Fe/C/PVDF electrodes has been found. Electric current affects the surface morphology and changes it from a mosaic structure to a monolith in atmosphere oxygen. The electrochemical properties of Fe/C/PVDF electrodes have been tested using cyclic voltammetry (CVA). The long air contact (for more than 3 hours) during electrochemical cycling changes the surface structure in the direction of decreasing crystallinity. The Fe/C/PVDF electrode can be charge in neutral solutions (pH ~7).

Key words: iron particle, active interphase, polyvinylidene fluoride, carbon, electrode.

INTRODUCTION. Using catalyst support materials is essential to nanostructured catalytic systems in many energy-transforming devices. Ideal catalyst carriers should possess the following properties: high conductivity, high surface area, low cost, electrochemical inertness, and stability. Noble metals (Pt, Ru, etc.) are considered to be the most active and stable materials for green hydrogen (GH) production but extremely high cost and limited natural abundance impede their wide industrial applications. Thus, nonplatinum active metals such as Fe, Ni, or Co as well as their alloys and composites have received great attention as electrocatalysts for GH because of their relatively low prices and availability [1]. Iron nanoparticle/polymer nanocomposites have recently become some of the most active research areas in the materials science and engineering [1–3]. Among the nanosized fillers

for these composites, iron and its oxides (FeO, Fe_2O_3, and Fe_3O_4) have attracted significant interest owing to their ability for redox reactions with huge heating effects and the ability to form surface interphases, leading to diverse applications in energy transforming devices [4–7]. For the polymeric matrix, polyvinylidene fluoride is a suitable semi-crystalline polymer owing to its remarkable thermal stability, good chemical resistance, and extraordinary pyroelectric and piezoelectric properties [8]. These properties, combined with its high elasticity, relative transparency, and ease of processing, make this thermoplastic polymer suitable for various technological applications. PVDF shows a complex structure including five distinct crystalline phases related to different chain conformations designed, known as α,β, δγ and ε phases [9,10]. Adding nanoparticles to a matrix such as PVDF can enhance its conductive performance and provide an advanced response by changing the nature and properties of the nanoscale filler [11]. This matrix forming an artificial interphase layer (a stable fluorine-doped amorphous carbon (CF) layer) for retaining uncontrollable metallic dendrites and side reactions is a highly desirable strategy for increasing coulombic efficiency and limiting long cycling stability of metal batteries [12]. Carbon-based materials have been used as catalyst supports for a long time due to their unique properties, such as physical stability, excellent conductivity, and high surface area. As the graphite anode in a lithium-ion battery, hard carbon is a widely accepted anode material for different batteries and capacitors. Initially, the PVDF binder was used in the electroactive hard-carbon anode. Nowadays, PVDF is the main component of composite electrodes. But this application of polyvinylidene fluoride exhibits poor reversibility of electrodes. Some authors attribute this impact to the formation of fluoropolymer - a product of the polymerization of tetrafluoroethylene molecules [13]. CVA measurements and electrochemical impedance spectroscopy data showed that improved catalytic activity towards GH was the result of an increase in the effective surface area, a change in surface features upon heating and the electrocatalytic synergism of Fe with other components of composites [1]. That is why the study of the appearance of new interphases on the iron surface in composite Fe/C/PVDF films and their impact on the electrocatalytic properties of composites are topical for the development of a new generation of energy storage for GH production.

EXPERIMENT AND DISCUSSION OF THE RESULTS. Preparation of Fe/C/PVDF electrode. A predetermined amount of iron powder (PGR 3.200.28-30) with a bulk density of 2.7 ± 0.2 g/cm3 (Ukraine) (Table 1), activated carbon BAU-A (Ukraine), and 1 % solution of PVDF in acetone (Sigma-Aldrich) stirred in an ultrasonic mixer up to homogeneity. Before mixing, powdered iron was treated with a solution of 1 M HNO3 to obtain oxides on the surface of the iron particles. Then, the electrode mass was pressed on a steel grid with a size of 1 cm^2.

Table 1.

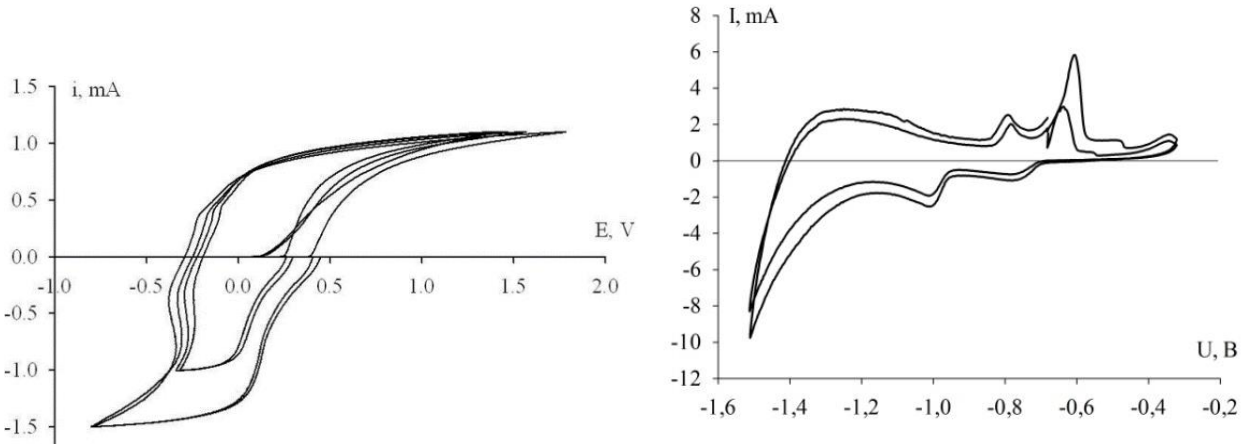
Mass fraction of impurities in powdered iron, wt. %

C	Si	Mn	S	P	O
0.05± 0.01	0.08± 0.02	0.20± 0.01	0.02± 0.02	0.02± 0.02	0.5± 0.01

An electrochemical module Autolab 30 PGSTAT301N Metrohm Autolab with 3-electrode cells was used for electrochemical studies. Powdered iron was the working electrode, the counter electrodes were platinum (Pt), carbon (C), and Ag/AgCl was reference electrode. Cyclic voltammograms (CVA) and open circuit potential (OCP) data were recorded at a potential scan rate of 0,1 and 50 mV/s in 0.1, 5 M solutions of NaOH and 1 M NaCl. Electrochemical impedance spectra were recorded in the potentiostatic mode both at open circuit potentials and at overpotentials of 100, 200, and 300 mV under H_2 evolution in a frequency range of 0.01 Hz ÷ 10^5 kHz with a constant ac voltage amplitude of 10 mV. The data of electrochemical impedance spectroscopy were processed by FRA and Zview software packages.

The micromorphological studies of composite samples and the quantitative microanalysis of the surface were performed on a scanning electron microscope Tescan Mira 3 LMU on the cathode with Schottky field emission and automatic measurement on images and on an energy dispersive spectrometer Oxford Instruments X-Max 80 mm^2 SDD (table). The analytical mode of the scanning microscope was used to determine the relationship between the microstructure and local thermal reactions on iron particles.

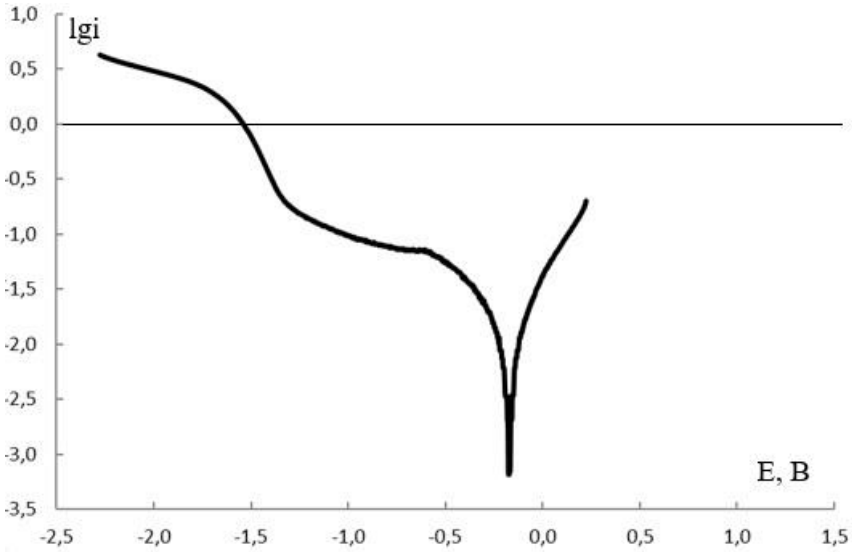
The CVA of the Fe/C/PVDF electrode in neutral and basic media has considerable differences in cathodic and anodic wave shapes and they have different potential ranges of stability (fig. 1 a, b). In the neutral media (NaCl), this range is 0.5 – 0.75 V with surface passivation in a wide potential range – 0.76 ÷ + 1.9 V vs NHE (fig 1 a) with increasing internal area of CVA.



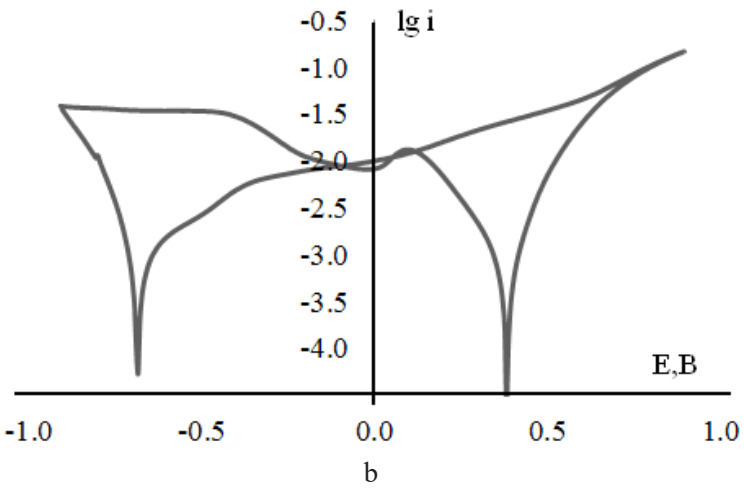
a b

Fig 1. CVA curves of iron powder electrode:
a – in 1 M NaCl (neutral media), b – in 0,1 M NaOH (alkali media).

The increase in these areas during the cycling of the electrode indicates its capability to charge. In alkaline media, the potential range of stability increased to 1.2 – 1.4 V without any passivation (fig 1 b, 2), which is explained by the formation of hydroxides on the surface [6]. Logarithmic dependences of current changes have specific differences in the electrochemical behavior of electrodes (Fig.2).



a



b

Fig. 2. Polarization curves of iron powder electrode in: a- 1 M NaCl; b - 0,1 M NaOH.

According to the Tafel equations, the Fe/C/PVDF electrodes have only one zero net current potential at – 0.173 V with further dissolution in a wide potential range from – 0.5 V to – 2.29 V in neutral media (fig.2, a). In alkaline electrolytes, the system has two zero net potentials at – 0.68 V and +0.35 V with a passivation range between – 0.23 and – 0.88 V (fig.2,b) which is associated with the impact of reversible redox reactions in Fe/Fe_xO_y (x = 0 ÷ 3)systems. This behavior is connected with active interphase generation on the electrode surface based on the thermodynamics of redox reactions (Table 2).

ISSN 2708-129X. Укр. хім. журн., 2023

Table 2.

Standard enthalpies of redox reactions with oxygen and carbon for iron and its oxides [15].

Equation of reaction	ΔH, kJ/M	Equation of reaction	ΔH, kJ/M
$2Fe + 3/2O_2 \rightarrow FeO$	-824	$FeO + C \rightarrow Fe + CO$	+100
$2FeO + 1/2\ O_2 \rightarrow Fe_3O_4$	-280	$FeO + CO \rightarrow Fe + CO_2$	+17
$Fe_2O_3 + Fe = 3FeO$	+14,7	$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$	+58
$Fe_2O_3 + Fe = 4FeO$	+16,8	$Fe_3O_4 + CO = 3FeO + CO_2$	+38

An analysis of Fe/C/PVDF electrode samples after 1 cycle showed a decrease in the amount of pure iron (Fe^0) by 0.24 mas.% which would, probably, be connected with the oxidation of iron in the reactions $Fe_2O_3+Fe= 3FeO$ and $Fe_2O_3+Fe= 4FeO$ under current load. The impact of oxygen has a good correlation with surface morphology. Cycling in the limited presence of oxygen brings the surface into a state of increasing particle size with retention of the mosaic surface structure (fig.3 a). If the electrode surface has long contact with air, this a mosaic structure becomes a monolayer structure (fig.3 b).

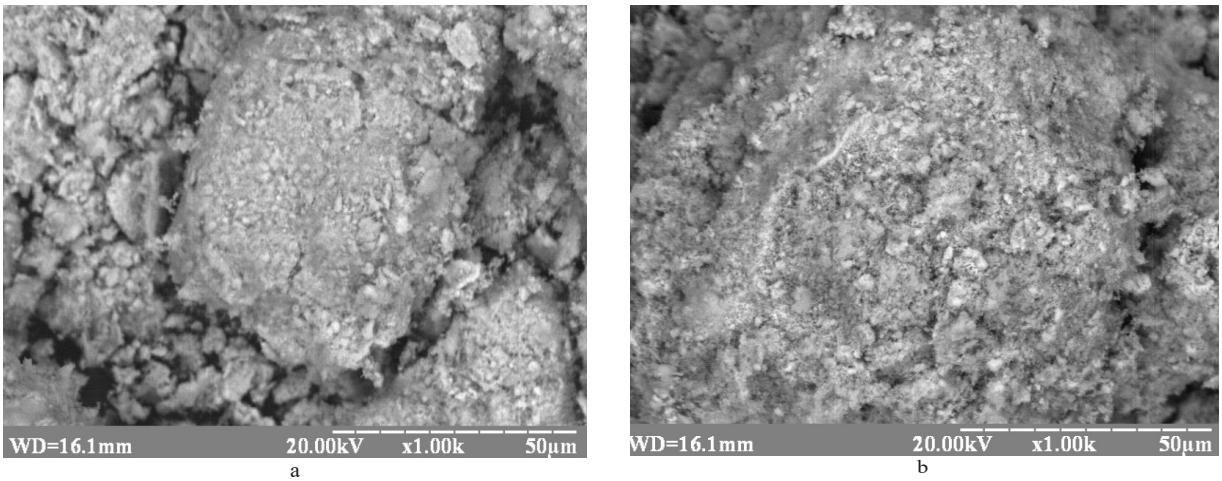


Fig. 3. SEM images of the surface of the electrode in the potential range – 0.23 ÷ -1.0 V: a – after cycling in the limited presence of oxygen; b – after cycling in the prolonged contact with air.

In this case, a transformation of surface morphology takes place. According to thermodynamic laws, the presence of an oxidized iron surface creates prerequisites for the implementation of several thermochemical reactions. Oxidation reactions with oxygen are exothermic, and reduction disproportionation reactions and reactions with carbon and carbon monoxide are endothermic (Table 3). Final calculations of the main molar enthalpies of iron reactions in these systems: Σ ΔHex– Σ ΔHend= -1504 + 444.5 = 1059.5 (kJ/M)

allows us to assume that external temperature influence should lead to a shift in thermodynamic equilibrium, i.e. can form local zones with the appropriate chemical potential. Thus, the presence of carbon and powdered iron in the electrode composition creates thermodynamic prerequisites for the appearance of temperature gradients on the electrode surface in the absence of electrical load. The enhancement of this effect is possible due to the introduction of impurities with low thermal conductivity good thermal stability and toughness. Polyvinylidene fluoride has all of these properties. On the other hand, PVDF is a well-known semicrystalline polymer in which the percentage of the crystalline phase remarkably affects almost all physical properties of polymers. So, the change in surface morphology can be the result of changes in PVDF crystallinity under temperature impact in the local zones near iron particles. [14].

Further analysis of oxygen content detected a difference in the oxygen content on the surface of iron particles and in the bulk of graphite (Fig.4, Table 3). This difference is related to the ability of Fe coated by Fe_3O_4 in the presence of graphite to induce the reduction of Fe^{3+} to Fe^{2+} with the generation of free high reactive oxygen. [16]. High by reactive oxygen is able to form -O–O- and C=O groups on PVDF mainly due to the exchange of F in C-F groups [17]. According to these properties, PVDF could have an initiator function to produce an active oxygen species.

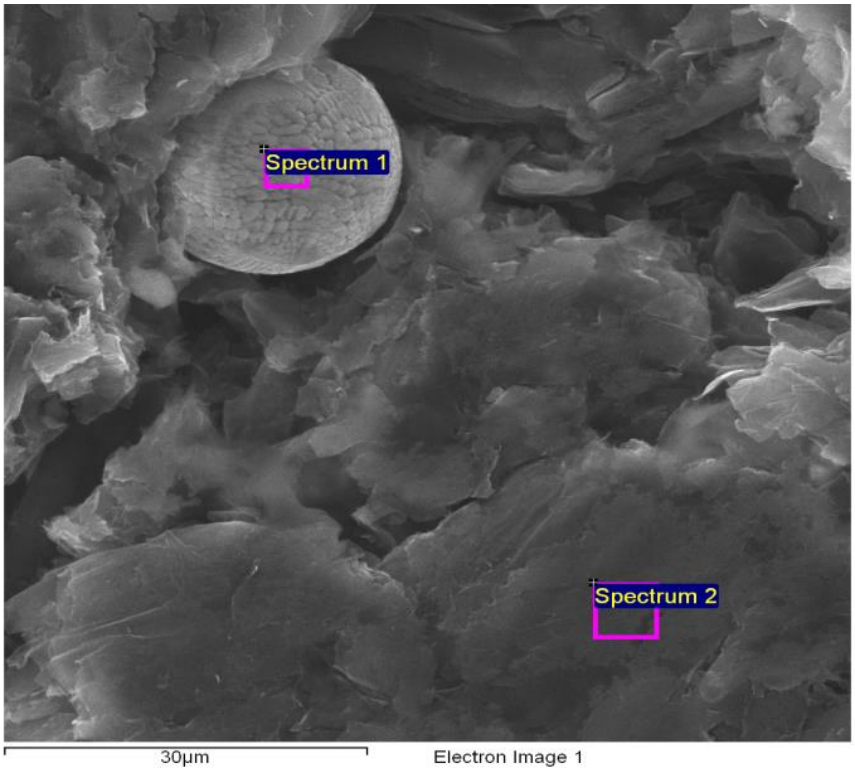


Fig.4. SEM image and analyzed zones on the surface of a Fe/C/PVDF film

Table 3.

The elementary composition of the composite film surface, wt.%

Zones of the sample	C	O	Fe	F	Ratio (formula)
Zone 1	23.21±2.1	48.83±0.3	26.23±0.5	0.77±0.5	FeC_4O_6
Zone 2	96.44±2.1	2.79±0.3	26.23±0.5	0.77±0.5	$Fe_3O\ C_{48}$

So, on the surface of iron particles forms a new interface (with a size of 30 ÷ 80 nm) (fig.4) saturated by active oxygen compounds with high mobility. A confirmation of the high mobility of oxygen species is the analysis of graphite in the bulk, where at a distance of more than 30 μm the presence of oxygen is found, but in smaller quantities. Also, in this region we detected Fe^0. If the presence of Fe_2O_3 takes place, the probability of the formation of Fe_3C increases in the graphite space. Thus, the simultaneous presence of proactive compounds of oxygen and iron carbide should significantly affect the formation of gradient phenomena and change the thermoelectric and electrochemical properties of the whole system.

CONCLUSIONS. The presence of an oxidized iron surface creates prerequisites for the realization of several thermochemical reactions and induces the appearance of the local zones with high temperatures. At these temperatures, the probability of the iron ions reduction in the presence of carbon and exchanging fluorine in C-F groups on oxygen with the formation of -O–O- and C=O groups on PVDF increases. In this case, iron particles become the centers of formation of a new active interphase with a high ability for redox transformation. Temperature and changing chemical structure are the factors of changing level of crystallinity of PVDF, which affect the surface morphology of Fe/C/PVDF electrodes. Under electric current impact such composition is able to change their electrochemical properties depending on the pH of the electrolyte. In neutral solutions (pH ~7), Fe/C/PVDF electrode has the property of a capacitor and has battery redox properties in alkaline solutions (pH~ 10).

AKNOLEDGEMENT. This work was supported by the National Academy of Sciences of Ukraine in the framework of project 0122U200794.

УТВОРЕННЯ АКТИВНОЇ ІНТЕРФАЗИ НА ЧАСТИНКАХ ЗАЛІЗА В ЕЛЕКТРОХІМІЧНИХ СИСТЕМАХ C/PVDF

Р. А. Пантелеймонов[1]., І. М. Щербатюк[2], К. Д. Першина[1,2]

[1]Інститут загальної та неорганічної хімії імені В. І. Вернадського НАН України, проспект Академіка Палладіна, 32/34, Київ 03142, Україна
[2]Міжвідомче відділення електрохімічної енергетики НАН України, проспект Академіка Вернадського, 38 А, Київ 03142, Україна
e-mail: radik20031@gmail.com

Можливість утворення активної міжфази на частинках заліза в середовищі C/PVDF була продиктована термохімічними реакціями заліза та оксидів заліза за присутності вуглецю. Композиція з полівініліденфторидом (PVDF) змінила окисно-відновну активність частинок заліза та зменшила кількість чистого заліза (Fe0) на 0,24 мас. %. Властивості поверхні різних композицій було охарактеризовано за допомогою скануючої електронної мікроскопії з аналітичним режимом для визначення зв'язку між мікроструктурою та локальними тепловими реакціями на поверхні частинки заліза. Було знайдено зв'язок між складом поверхні, морфологією та електрохімічною поведінкою електродів Fe/C/PVDF. Електричний струм впливає на морфологію поверхні та змінює її з мозаїчної структури на моноліт за присутності кисню повітря. Тривалий контакт повітря (понад 3 години) під час електрохімічного циклування змінює структуру поверхні в бік зниження кристалічності. Електрод Fe/C/PVDF може заряджатися в нейтральних розчинах (pH ~7).

Ключові слова: частинка заліза, активна міжфаза, полівініліденфторид, вуглець, електрод.

REFERENCES

1. Moeez I., Susanto D., Chang W., Lim H. D., & Chung K. Y. Artificial cathode electrolyte interphase by functional additives toward long-life sodium-ion batteries. *Chemical Engineering Journal*. 2021. 425: 130547. https://doi.org/10.1016/j.cej.2021.130547
2. Bock D. C., Waller G. H., Mansour A. N., Marschilok A. C., Takeuchi K. J., & Takeuchi E. S.. Investigation of solid electrolyte interphase layer formation and electrochemical reversibility of magnetite, Fe3O4, electrodes: a combined X-ray absorption spectroscopy and X-ray photoelectron spectroscopy study. *The Journal of Physical Chemistry C*. 2018. **122**(26): 14257–14271. https://doi.org/10.1021/acs.jpcc.8b01970
3. Bruck A. M., Gannett C. N., Bock D. C., Smith P. F., Marschilok A. C., Takeuchi K. J., & Takeuchi E. S. The electrochemistry of Fe3O4/polypyrrole composite electrodes in lithium-ion cells: the role of polypyrrole in capacity retention. *Journal of The Electrochemical Society*. 2016. **164**(1): A6260. doi: 10.1149/2.0361701jes
4. Naber W. J. M., Faez S., & van der Wiel W. G. Wilfred Gerard. Organic spintronics. *Journal of Physics D: Applied Physics*. 2007. **40**(12): R205. doi: 10.1088/0022-3727/40/12/R01
5. Tsonos C., Zois H., Kanapitsas A., Soin N., Siores E., Peppas G. D., ... & Psarras G. C. Polyvinylidene fluoride/magnetite nanocomposites: Dielectric and thermal response. *Journal of Physics and Chemistry of Solids*. 2019. **129**: 378–386. https://doi.org/10.1016/j.jpcs.2019.01.025
6. Kravchenko O. V., Pershina K. D., Panteleymonov R. A., & Potapenko O. V. Electrochemical Properties of Powder Iron/Carbon System in Basic Solution. *Materials Today: Proceedings*]. 2019. **6**: 65–72. https://doi.org/10.1016/j.matpr.2018.10.076
7. Boichuk O., Pershina K., Riabokin O., Kravchenko A., & Panteleimonov R. Thermo-galvanic effects in a non-isothermal element based on the of iron-carbon compositional electrode and alkaline electrolyte. *Ukrainian Chemistry Journal*. 2020. **86**(4): 108–117 https://doi.org/10.33609/2708-129X.86.4.2020.108–117
8. Sencadas V., Moreira M. V., Lanceros-Méndez S., Pouzada A. S., & Gregório Filho R. α-to β

Transformation on PVDF Films Obtained by Uniaxial Stretch. In: *Materials science forum*. Trans Tech Publications Ltd, 006. **514**: 872–876. https://doi.org/10.4028/www.scientific.net/MSF.514-516.872

9. Broadhurst M.G., Davis G.T., McKinney J.E., & Collins R.E. Piezoelectricity and pyroelectricity in polyvinylidene fluoride—A model. *Journal of applied physics*. 1978. **49**(10): 4992–4997. https://doi.org/10.1063/1.324445
10. Lovinger Andrew J. Annealing of poly (vinylidene fluoride) and formation of a fifth phase. *Macromolecules*. 1982. **15**(1): 40–44. https://doi.org/10.1021/ma00229a008
11. Ramazanov M. A., Alizade R. A., Maharramov A. M., Hajiyeva F. V., Sultanova J. R., & Shirinova H. A. Theoretical and experimental study of the magnetic properties and size of distribution of PVDF+ Fe based nanocomposites. *Journal of Inorganic and Organometallic Polymers and Materials*. 2018. **28**: 2179–2186. https://doi.org/10.1007/s10904-018-0863-2
12. Wang H., Chen Y., Yu H., Liu W., Kuang G., Mei L., ... & Chen L. A Multifunctional Artificial Interphase with Fluorine-Doped Amorphous Carbon layer for Ultra-Stable Zn Anode. *Advanced Functional Materials*. 2022. **32**(43): 2205600 https://doi.org/10.1002/adfm.202205600
13. Ramaprabhu S., & Ajay P. V. *Handbook of Sodium-Ion Batteries*. 2023. 323–344.
14. Xu H.P., Dang Z.M. Electrical property and microstructure analysis of poly (vinylidene fluoride)-based composites with different conducting fillers. *Chemical physics letters*. 2007. **438**(4–6): 196–202 https://doi.org/10.1016/j.cplett.2007.02.076
15. Galvez M. E., Loutzenhiser P. G., Hischier I., & Steinfeld A. CO_2 splitting via two-step solar thermochemical cycles with Zn/ZnO and FeO/Fe3O4 redox reactions: thermodynamic analysis. *Energy & Fuels*. 2008. **22**(5): 3544–3550. https://doi.org/10.1021/ef800230b
16. Correia D. M., Ribeiro C., Sencadas V., Botelho G., Carabineiro S.A.C., Ribelles J. G., & Lanceros-Méndez S. Influence of oxygen plasma treatment parameters on poly (vinylidene fluoride) electrospun fiber mats wettability. *Progress in Organic Coatings*. 2015. **85**: 151–158 https://doi.org/10.1016/j.porgcoat.2015.03.019
17. Ross G. J., Watts J. F., Hill M. P., & Morrissey P. Surface modification of poly (vinylidene fluoride) by alkaline treatment1. The degradation mechanism. *Polymer*. 2000. **41**(5): 1685–1696. https://doi.org/10.1016/S0032-3861(99)00343-2

Стаття надійшла 05. 02. 2023.