Supplementary Information

Electrocatalytic properties of a carbothermically obtained composite based on vanadium nitridophosphide in the hydrogen evolution, oxygen evolution, and oxygen reduction reactions

Denys O. Mazur, Olena O. Pariiska, Yaroslav I. Kurys*, Vyacheslav G. Koshechko

L.V. Pisarzhevskii Institute of Physical Chemistry of the National Academy of Sciences of Ukraine, 31 Nauky Pr., Kyiv 03028, Ukraine

*E-mail: yarkurys@ukr.net

1. Preparation of Phosphoric Acid-Doped Polyaniline (PAni·H_3PO_4) and its Pyrolysis Product – N,P-Doped Nanocarbon (N,P-C)

To a solution of 6 mL of aniline in 87 mL of 2M H_3PO_4, 18.92 g of $(NH_4)_2S_2O_8$ dissolved in 33 mL of 2M H_3PO_4 was added with stirring. This rapidly led to the formation of a dark-green precipitate, characteristic of the doped electrically conductive form of PAni – emeraldine salt, in about 1 minute. The precipitate was filtered after 1 hour, thoroughly washed with 2M H_3PO_4 and acetonitrile, then air-dried to obtain PAni·H_3PO_4.

To obtain N,P-C, which does not contain vanadium-containing particles, the PAni·H_3PO_4 was transferred to a ceramic crucible and placed in a tube furnace, which was purged with argon for 15 minutes. After this, the PAni·H_3PO_4 underwent heat treatment in a flow of argon at 900°C for 3 hours, followed by cooling the resulting carbonization product to room temperature in an argon atmosphere. Subsequently, the pyrolysis product was treated with 0.5 M H_2SO_4 (80°C, 1 hour), filtered, washed with water (until pH ~ 7), and dried in a drying oven at 90°C.

2. Electrochemical Characterization: Additional Details

The Tafel slope (b) was calculated using the Tafel equation (**S1**):

$$\eta = a + b\lg j = \frac{2.3RT}{\alpha nF}\lg j_0 + \frac{2.3RT}{\alpha nF}\lg j, \qquad \textbf{(S1)},$$

where, η – overpotential, mV; j – current density (in ORR case, correction for mass transfer was introduced $j \times j_d/(j_d-j)$); mA/cm^2; j_0 – exchange current density, mA/cm^2; b – Tafel slope, mV decade^{-1}; α – transfer factor; n – number of electrons, involved in the electrochemical reaction; F – Faraday constant; R – universal gas constant; T – temperature, K.

To calculate the number of electrons involved in the reduction of 1 molecule of oxygen (n), the yield of hydrogen peroxide ($H_2O_2\%$), and to determinate half-wave potentials were used the equations **S2**, **S3**, and **S4**, respectively:

$$n = 4\frac{I_d}{I_d + \frac{I_r}{N}} \qquad \textbf{(S2)}$$

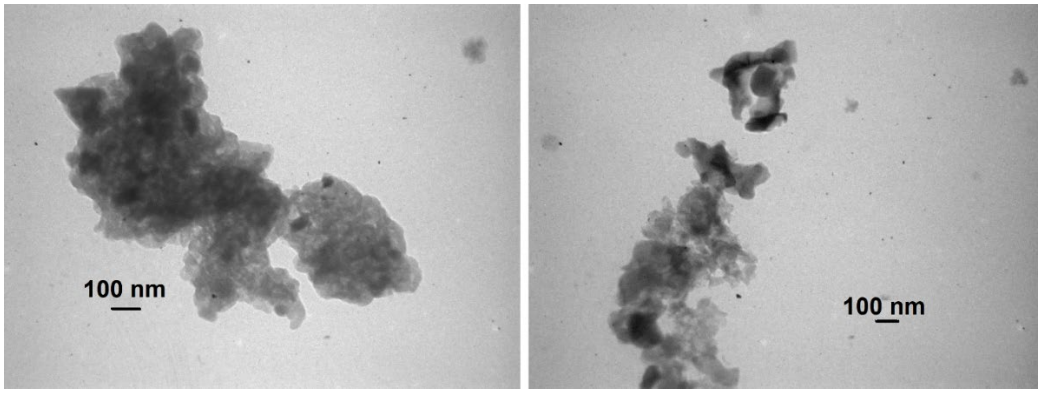
$$H_2O_2\% = 200\frac{\frac{I_r}{N}}{I_d + \frac{I_r}{N}}, \qquad \textbf{(S3)}$$

where I_d is the disk current, I_r is the ring current, and N is the correction factor.

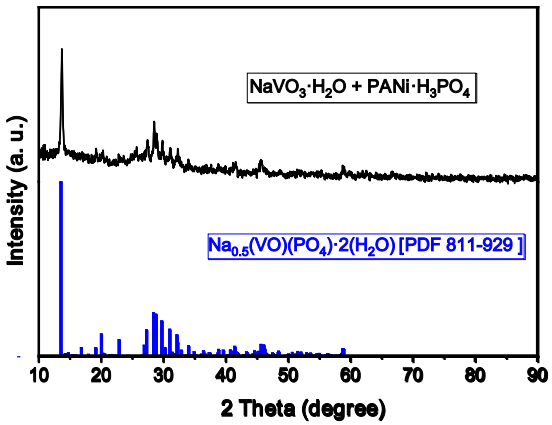
$$E = E_{1/2} + 2.3\frac{RT}{\alpha nF}\lg\frac{j}{j_d - j} \qquad \textbf{(S4)},$$

where $E_{1/2}$ – half-wave potential, V; j and j_d – current density and diffusion current density, correspondingly, A/cm^2; n – number of electrons, involved in the electrochemical reaction; α – transfer factor; F – Faraday constant; R – universal gas constant; T – temperature, K.

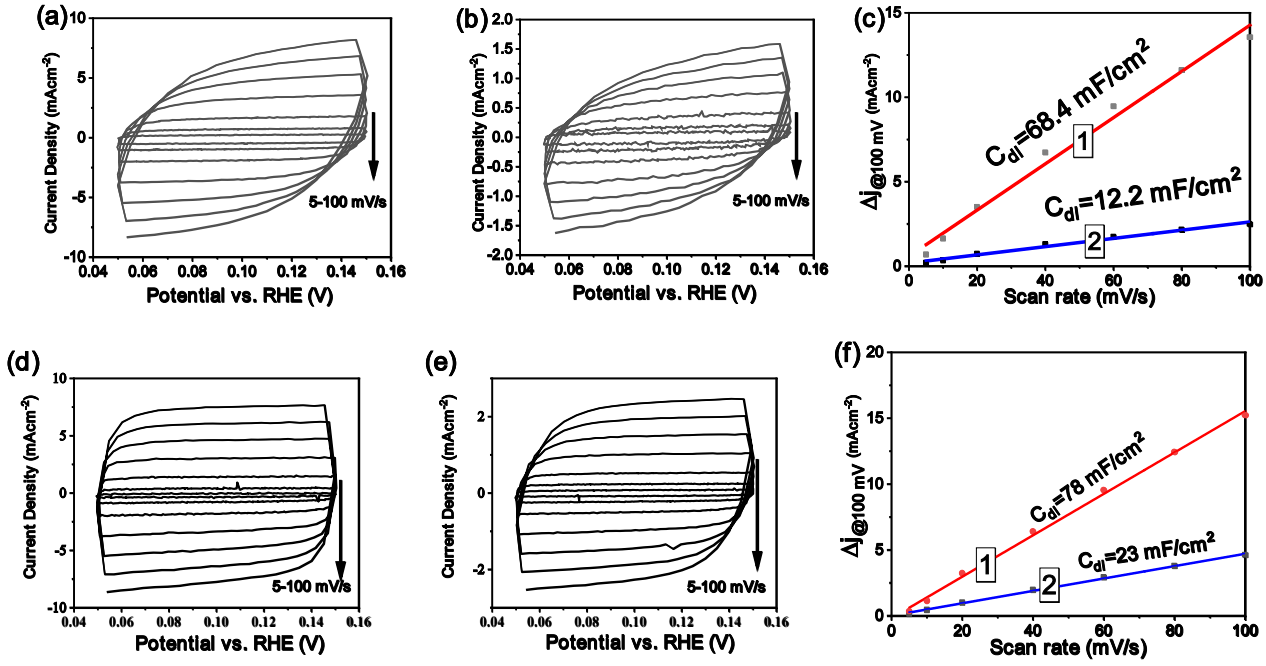
3. Fig. S1. TEM images of the V_5NP_3/N,P-C composite



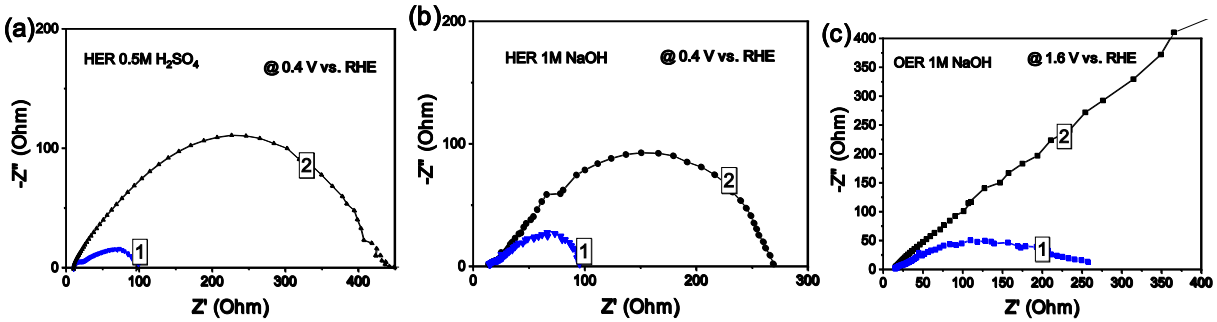
4. Fig. S2. XRD-patterns of the precursor (dried mixture of $NaVO_3 \cdot H_2O$ with $PANi \cdot H_3PO_4$) and $Na_{0.5}(VO)(PO_4) \cdot 2H_2O$ [PDF 811-929]



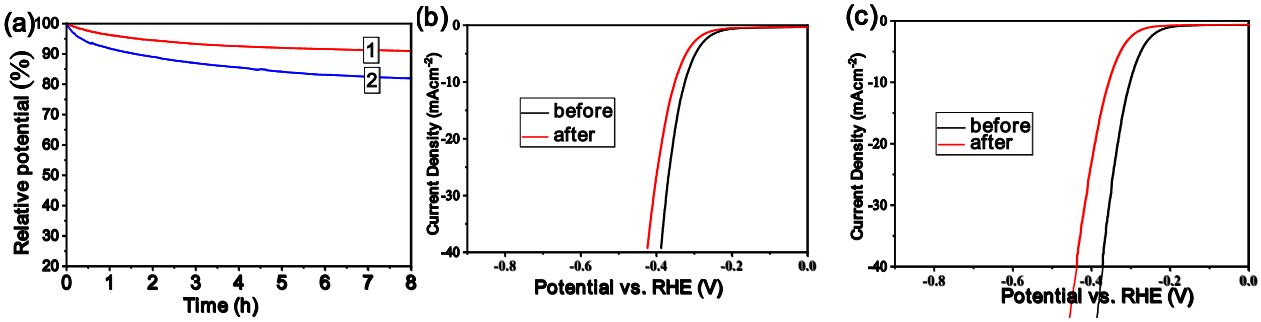
5. Fig. S3. Cyclic voltammetry plots of V_5NP_3/N,P-C (a) and N,P-C (b) with varying scan rates from 5 to 100 mV s^{-1} and C_{dl} measurement (c) of V_5NP_3/N,P-C (1) and N,P-C (2) in 0.5 M H_2SO_4 (a-c) and in 1 M NaOH (d-f).



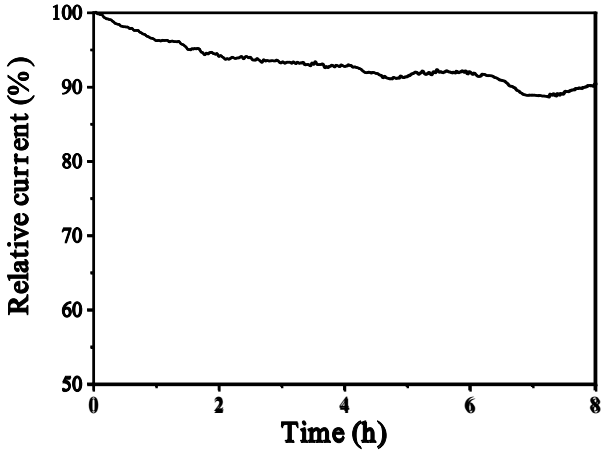
6. Fig. S4. Nyquist plots for V_5NP_3/N,P-C (1) and N,P-C (2) in 0.5 M H_2SO_4 (a) and 1.0 M NaOH (b) at 0.4 V vs. RHE, and in 1.0 M NaOH at 1.6 V vs. RHE (c).



7. Fig. S5. Chronopotentiometry plots (a) at the constant current density of 10 mA cm^{-2} in 0.5 M H_2SO_4 (2) and 1.0 M NaOH (1) for V_5NP_3/N,P-C. HER polarization curves for V_5NP_3/N,P-C recorded before and after the chronopotentiometric test in 0.5 M H_2SO_4 (c) and 1.0 M NaOH (b)



8. Fig. S6. Chronoamperometry test with the potential holding at 0.6 V in O_2-saturated 1.0 M NaOH for V_5NP_3/N,P-C



9. Electrochemical Characteristics of Various Catalysts for HER, OER, and ORR

Table S1. Electrochemical Characteristics of Various Catalysts for HER

Catalyst	Electrolyte	Catalyst loading (mg cm^{-2})	η_{10} (mV)	Tafel (mV dec^{-1})	ref
VN	1 M KOH	0.5	>400	96	1
VN@NC	1 M KOH	1.28	425	130.29	2
PSC-VN	1 M KOH	-	74.67	68.3	3
	0.5 M H_2SO_4		~125*	71.14	
PPC-VN	1 M KOH		150.66	178.5	
	0.5 M H_2SO_4		~160*	100.46	
VN@NC	1 M KOH	0.94	485	126	4
VN-NF	1 M KOH	-	163	121	5
VN	1 M KOH	-	373	110	6
VN-P			302	101	
VP@CC	1 M KOH	-	360	121	7
VN@NC	1 M KOH	0.89	~580*	-	8
	0.5 M H_2SO_4		~1075*	-	
VN	1 M KOH	0.4	199	133.6	9
VN/NC	1 M KOH	-	347	223	10
VN	1 M KOH	0.56	476	165	11
VN/NF	1 M KOH	-	291	125	16
V_5NP_3/N,P-C	**1 M NaOH**	**1.15**	**304**	**91**	**This work**
	0.5 M H_2SO_4		**325**	**91**	

* - Calculated based on the HER polarization curves presented in the respective works.

Table S2. Electrochemical Characteristics of Various Catalysts for OER

Catalyst	Electrolyte	η_{10} (mV)	Tafel (mV dec^{-1})	ref
VN	1.0 M KOH	458	-	6
VN-P		401	-	
VN@NC	0.1 M KOH	>770	473	15
VN nanosheets	1.0 M KOH	~570	-	18
VP_2/NF	1.0 M KOH	~420	141	16
V_5NP_3/N,P-C	**1.0 M NaOH**	**290**	**241**	**This work**

Table S3. Electrochemical Characteristics of Various Catalysts for ORR

Catalyst	Electrolyte	Onset potential (V vs RHE)	Half-wave potential (V vs RHE)	Electron transfer numbers(n)	Tafel (mV dec^{-1})	ref
VN	0.1 M KOH	0.85	0.72	-	115	11
VN/NC/C	0.1 M KOH	0.85	0.75	3.80	75.54	12
NGT-V NC-V	0.1 M KOH	0.88 0.89	0.79 0.80	- -	70.4 72.9	13
VN MFs	0.1 M KOH	~0.82	~0.62	3.9	-	14
VN	0.1 M KOH 0.1 M $HClO_4$	<0.75 No activity	- -	3.2 -	-	17
VN/GC	0.1 M $HClO_4$	0.67	0.51	-	-	19
V_5NP_3/N,P-C	**1.0 M NaOH**	**0.89**	**0.82**	**3.30**	**61**	**This work**

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