Supplementary data.

Pt-Mo/C, Pt-Fe/C, and Pt-Mo-Sn/C Nanocatalysts Derived from Cluster Compounds for Proton Exchange Membrane Fuel Cells

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MEA can be used for evaluation of the electrochemically active surface area (ECSA) of Pt in the catalyst layer by measurements of electrochemical adsorption/desorption of hydrogen. For that, working electrode compartment of the studied MEA containing PtMo/C catalyst (working electrode) was supplied with humidified nitrogen, while humidified hydrogen was supplied to the compartment of the counter electrode, containing Pt/C catalyst. Since overvoltage at the counter electrode (Pt/C) in the presence of hydrogen and protons is negligible, scanning of the cell voltage in the potential range 0.05-1.3 V, results in electrochemical adsorption and desorption of hydrogen on the PtMo/C catalyst and is accompanied by redox processes involving Mo species of different valence.

Cyclic voltammetry at room temperature under conditions described is shown in Figure S1. The curve obtained differs from the voltammetry of hydrogen adsorption/desorption on Pt by the presence of a pair of redox peaks (I) and (II). These peaks can be ascribed to redox processes of MoO_x-type species.

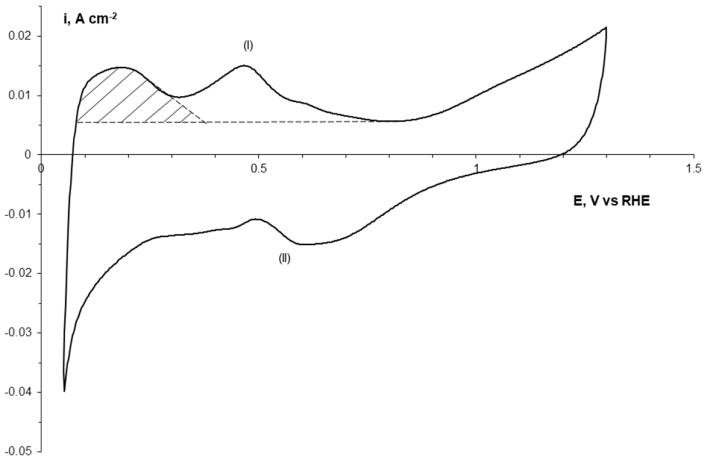

Figure S1. Cyclic voltammetry of hydrogen adsorption/desorption at PtMo/C catalyst measured at room temperature with MEA, containing PtMo/C at the working electrode. Voltage scan rate is 50 mV s^{-1}.

Although the curve seems complicated due to the presence of these redox peaks, it can be used for rough estimation of the platinum ECSA in the PtMo/C catalyst. Using the charge in the dashed area (see Figure S1) and assuming adsorption of one hydrogen atom per single surface Pt atom [S1], the value of platinum ECSA ~66 $m^2\ g^{-1}_{Pt}$ is obtained, which corresponds to evaluation of the Pt ECSA by TEM measurements.

Table S1. XRF Spectroscopy study of the as- prepared catalysts PtFe/C, PtMo/C and catalysts subjected to 50 cycles of voltammetry in a three electrode cell.

Samples PtFe and PtMo
Date 17/2/2022 3:50:05 PM
Result type Atomic[%]

Spectrum Label	Calc	Pos.X	Pos.Y	Pos.Z
15keV P4	YES	-1566	23684	0

Sample	All results in atomic[%]			
	Pt	Fe	Mo	Total
Pt-Fe as-prepared	48.89	51.11		100
Pt-Mo as-prepared	39.89		60.11	100
Pt-Fe after	52.90	47.10		100
Pt-Mo after	50.9		49.1	100

The voltammetry measurements were performed at a scan rate of 0.05V s^{-1} in the potential range 0 - 1.2 V vs RHE in argon purged 0.5M H_2SO_4 at room temperature. The

thin layers of PtFe/C, PtMo/C catalyst were coated on the surface of a glassy carbon disk electrode.

References.

S1. Conway, B.; Angerstein-Kozlowska A.; Sharp W.B.A. Temperature and pressure effects on surface processes at noble metal electrodes. Part 1.—Entropy of chemisorption of H at Pt surfaces. *J. Chem. Soc. Faraday Trans.* **1978**, *1*, 1373-1389. https://doi.org/10.1039/F19787401373.