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DOI: 10.15199/40.2024.8.1

# Application of heteropoly compounds with Keggin structure in corrosion protection and Ni-MH cell technology

## Zastosowanie heteropolizwiązków o strukturze Keggina w ochronie przed korozją i technologii ogniw Ni-MH

Heteropolyacids (HPA) and their salts are a group of chemical compounds that arouse the interest of many researchers due to the variety of properties and applications. These compounds are characterized by, among other things, high proton mobility, as well as the ability to accept and release electrons. HPAs are extensively studied especially in the design of various functional catalysts. The area of their application is constantly growing due to the possibility of modifying their chemical composition.

This work presents the basic areas of research on Keggin-type heteropoly compounds (HPC), with particular emphasis on their catalytic and anti-corrosion properties, to assess the possibility of using HPAs in Ni-MH cell technology. Analysis of the available literature confirmed our assumption that these are promising compounds offering both chemists and materials scientists many cognitive and application possibilities. Literature examples indicate that HPA should fulfil two important tasks: catalyse the charging/discharging processes of hydride electrodes in Ni-MH cells and inhibit corrosion processes leading to the degradation of the electrode material.

**Keywords:** heteropolyacids, corrosion protection, electrochemical cells, electrocatalytic properties

Heteropolikwasy (HPK) i ich sole to grupa związków chemicznych, która ze względu na różnorodność właściwości i zastosowań wzbudza zainteresowanie wielu badaczy. Związki te charakteryzują się między innymi wysoką mocą i ruchliwością protonów, a także zdolnością do przyjmowania i uwalniania elektronów. HPK są badane zwłaszcza pod kątem projektowania różnych katalizatorów funkcjonalnych. Zakres ich zastosowania stale się zwiększa ze względu na możliwość modyfikacji ich składu chemicznego.

W pracy zostały opisane podstawowe obszary badań heteropolizwiązków (HPZ) o strukturze Keggina. Uwzględniono ich właściwości katalityczne i antykorozyjne w celu dokonania oceny możliwości wykorzystania HPK w technologii ogniw Ni-MH. Analiza literatury przedmiotu potwierdziła założenie, że związki te mają duży potencjał aplikacyjny i stanowią interesujący przedmiot badań zarówno dla chemików, jak i materiałoznawców. Z publikacji dotyczących tego zagadnienia wynika, że HPK powinny spełniać dwa ważne zadania: katalizować procesy ładowania i rozładowania elektrod wodorkowych w ogniwach Ni-MH oraz inhibitować procesy korozyjne, prowadzące do degradacji materiału elektrodowego.

**Słowa kluczowe:** heteropolikwasy, ochrona przed korozją, ogniwa elektrochemiczne, właściwości elektrokatalityczne

### 1. Introduction

Heteropolyacids (HPA) are well-known and widely used in many areas of industry and the laboratory. They are of interest in the fields of catalysis, electrochemistry, biochemistry, photochemistry

and biomedicine. Numerous basic research activities are underway to synthesise, structurally analyse and evaluate the reactivity of new heteropoly compounds. Although different types of heteropolyacid structures exist, Keggin-type HPAs are most commonly

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■ Received / Otrzymano: 8.05.2024. Accepted / Przyjęto: 27.06.2024

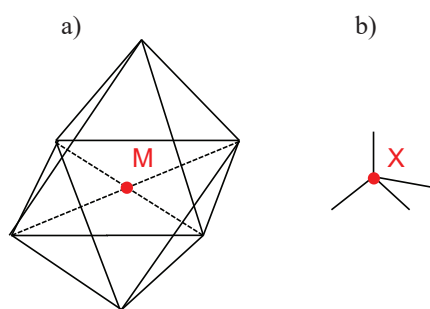


Fig. 1. Basic elements of the heteropolyacid skeleton: a) octahedral groups, b) tetrahedral groups

Rys. 1. Podstawowe elementy budowy szkieletu heteropolikwasu: a) ugrupowania oktaedryczne, b) ugrupowania tetraedryczne

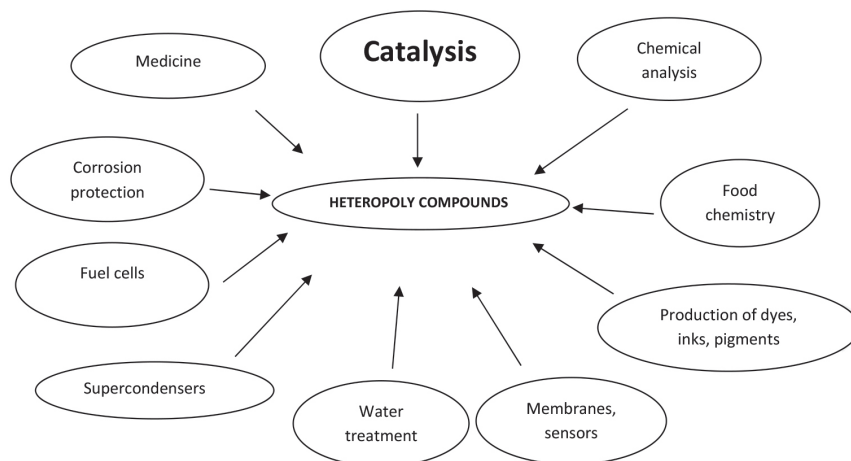


Fig. 2. Examples of the use of heteropoly compounds

Rys. 2. Przykłady zastosowania heteropolizwiązków

used due to their commercial availability, chemical stability and the possibility of modifying their chemical composition for specific applications.

Considering recent developments in the synthesis, characterisation and application of Keggin-structured HPAs, we would like to draw particular attention to the new possibilities of using this group of compounds in nickel-metal hydride (Ni-MH) batteries, both as electrocatalysts of the  $\text{H}_2\text{O}/\text{H}_2$  system and as corrosion inhibitors of the electrode material.

This review presents a general characterisation of Keggin-type heteropolyacids. The main areas of application of heteropoly compounds (HPC) are discussed, taking into account their structure and properties. The focus is particularly on the electrochemical and electrocatalytic properties and the potential use of HPAs in energy storage and conversion devices. Based on examples from the literature, the anti-corrosion properties of HPCs were also evaluated in the context of the production of protective coatings on hydride electrode (MH) material particles.

## 2. General characteristics of Keggin-type HPCs

Heteropoly compounds are a group of inorganic compounds comprising heteropolyacids and their salts (polyoxometalates) with anions built mostly from octahedral  $\text{MO}_6$  units (Fig. 1a) with common edges and/or corners that surround a tetrahedrally coordinated oxide heteroanion  $\text{XO}_4^{n-}$  (Fig. 1b). The central X atom (heteroatom) is usually a phosphorus or silicon atom, while the M metal atoms are usually tungsten, molybdenum or vanadium. More than 60 different elements of the periodic table can be used as heteroatoms [1]. This flexibility leads to a wide variety of structures, compositions and properties of HPCs. Among the wide variety of heteroatoms, Keggin-type HPCs ( $[\text{XO}_4]^{n-}\text{M}_{12}\text{O}_{36}$ ) are the most stable and readily available [1–3].

Heteropolyacids dissolve very well in polar solvents such as water, alcohols, ketones or ethers. They can form various phase systems, e.g. homogeneous liquid, liquid/solid, gas/solid, liquid/liquid. They are highly stable in acidic media and dissociate or may dissociate completely in solution in alkaline and neutral media.

They show the ability to adsorb on solid substrates such as activated carbon or silicon (IV) oxide [4–6]. Reduced forms of HPAs, containing molybdenum and vanadium, are referred to as “heteropoly blues” because of the intense blue colour they produce. Supplying electrons to heteropoly blues causes them to turn into “heteropoly browns” [7]. A highly desirable feature of HPAs is their ability to conduct ions, due to their hydrophilic properties and the significant oxygen content on their surface [8]. They can be used in hetero- and homogeneous catalysis [9]. A feature of polyanions is their poor solvation ability due to their large size, low charge density and high symmetry. The oxidation properties of HPAs are dependent on the type of ligand and the central atom [4]. Aqueous solutions of HPAs are much stronger than mineral acids such as  $\text{HNO}_3$ ,  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ . HPAs are characterised by “structural flexibility”, meaning that water and other organic polar molecules can “enter” and “exit” the crystal, accompanied by a change in the volume of the crystal cell. Heteropolyacids have the ability to catalyse the adsorption of polar molecules on the surface and inside the crystal, so that they behave as concentrated solutions. In the case of non-polar molecules, there is only an interaction with the surface of the catalyst. The activity of Keggin acids depends on acid strength, oxidation potential, thermal stability and also hydrolytic stability [4].

## 3. Applications of Keggin-type HPCs

### 3.1. Areas of application of Keggin-type HPCs

The practical applications of heteropolyacids are very broad. Fig. 2 shows examples of the application areas of HPCs. Most of the available publications and patents on heteropolyacids and their salts are related to their catalytic activity. HPCs can be used in fuel cells, in capacitors, as corrosion inhibitors or in electrochromic materials. In addition, they are used in chemical analysis, in medicine, as well as in the production of dyes or gas and moisture sensors.

Due to their high redox activity, selectivity, separation properties and durability in aqueous solutions, HPAs can be used both in acid catalysis and as redox catalysts. Heteropoly compounds having tungsten (VI and V) or molybdenum (VI, V) in their structure show the best performance as catalysts in redox processes due to their

ability to undergo multiple transitions from the oxidised to the reduced state [10]. An unquestionable advantage of HPCs used as catalysts is their considerable thermal stability, which makes them suitable also for use as high-temperature catalysts. They are characterised by a small surface area ( $<10\text{m}^2/\text{g}$ ), meaning that, being catalysts, they are most often deposited on carriers (e.g. carbon, inorganic materials or a polymer matrix) [11].

In order to improve the performance of fuel cells in terms of their instability, or the high corrosivity of the electrolyte and the short life of the cell [12], HPAs began to be used as additives to increase catalyst efficiency, membrane additives to increase the ionic conductivity of the electrolyte and as stand-alone catalysts. It has been found that HPAs can be introduced into cells in several ways: incorporation into the ion exchange membrane, immobilisation on the electrodes, or solvation in the electrolyte [1]. In order to increase the energy density of electrochemical capacitors, HPCs have been used as active materials, including by depositing heteropolyanions on the surface of carbon electrodes [13–15].

HPCs, due to their uniform dimensions at the “nano” scale, have the ability to transmit light, which makes them attractive as molecular pigments [16]. They also exhibit photocatalytic abilities to degrade toxic dyes containing aromatic rings, or nitrogen groups used in printing and dyeing of textiles [17]. The combination of HPCs with ionic surfactants allows them to be used as a purifier from toxins such as heavy metals, bacteria, organic dyes or radionuclides [18].  $\text{SiW}_{12}\text{O}_{40}^{4-}$  is used as a neutraliser of secondary metabolites produced by cyanobacteria [19]. HPAs interact with a wide range of proteins and enzymes and also show antiviral and anticancer activity [7]. Due to their hydrophilic properties, reversible proton conductivity with changes in moisture content and the ability to incorporate HPAs into a conductive polymer matrix, they can serve as high-performance moisture-detecting electrolytes [8].

### 3.2. Use of heteropoly compounds in corrosion protection

Katsoulis, in his review paper [7], extensively describes the potential use of heteropoly compounds for both corrosion inhibition of steel and non-ferrous metals such as aluminium and its alloys, zinc and cadmium. As we learn from the article [7], compositions based on synthetic resins and inorganic binders, which contained HPC as anticorrosive pigments, were already known in the 1980s and 1990s. HPCs containing organic cations also exhibit anticorrosive properties [20, 21]. Hydrophobic coatings consisting of organic cations and inorganic heteropolyanions, in addition to effectively inhibiting the corrosion of stainless steel in acidic environments [20], can also protect building stones by slowing their degradation [21]. The use of the organic-inorganic hybrid  $(n\text{C}_7\text{H}_{15})_4\text{N}_5[\text{PW}_{11}\text{O}_{39}\text{Cu}(\text{H}_2\text{O})]$  provided ~99% protection efficiency for stainless steel in a sulphuric acid environment, in the temperature range of 25–40°C [20]. As shown in [22], also the introduction of organometallic groups can enhance the protective function of HPCs and stabilise their structure. It is also possible to produce a hybrid material by combining HPCs with conductive polymers. Conductive polymers doped with HPC can provide effective corrosion protection for both carbon [23], stainless [24, 25] and low-alloy steels [26] in the presence of halide ions. The large volume and high charge of polyoxoanions immobilised in the polymer matrix makes their dif-

fusion coefficient low, which prevents their exchange with anions present in solution. Thus, these materials represent a promising and effective barrier against pitting corrosion [23–26].

HPCs can slow down corrosion by forming a protective layer on the metal surface that prevents contact with corrosive agents or modify the electrochemical properties of the protected metal by reducing the rate of both cathodic and/or anodic reaction (Table 1). Literature examples suggest that the mechanism of the protective action of HPCs is due to a combination of the oxidising properties of heteropolyacids and their ability to form insoluble salts with large cations. Compared to other inhibitors, such as chromates, HPCs have low toxicity; moreover, they accept electrons without significant structural change.

As can be seen from Table 1, HPCs have mostly been used to protect ferrous metals in low pH environments. The wide applicability of polyoxometalates as corrosion inhibitors is due to their high durability and affinity to the metal surface in acidic solutions. This leads to greater corrosion inhibition efficiency and a reduction in the amount of HPCs needed to achieve the desired effect. It has recently been shown that HPCs are not the best alternative corrosion inhibitors for aluminium alloys in alkaline media [27], which may be due to their lack of stability and therefore effective action in high pH electrolytes.

It can be speculated that the incorporation of HPCs into nanocomposite hydride electrodes by immobilisation on a carbon substrate may provide them with stability also in alkaline environments, while the combination of the oxidising nature of the various HPAs with their ability to form complexes with metals [28] would provide effective corrosion inhibition. Further research is needed to confirm this hypothesis and identify the nature of the resulting layers and to know their corrosion inhibition effect.

### 3.3. Keggin-type HPC applications in electrochemical energy conversion and storage devices

Heteropolyacids undergo fast, reversible electrochemical reactions because they have transition metal atoms in their structure at the highest oxidation levels that can be reduced and large amounts of mobile protons. Due to their reversible, fast and multi-electron redox reactions and very good solubility in polar solvents, they can be an alternative to vanadium compounds in redox flow batteries [29, 30].

Modification of electrodes with HPCs results in improved kinetics of electron exchange reactions making them ideal for use in catalytic electrooxidation or electroreduction processes. Suitably selected heteropoly compounds can be used both as catalysts/mediators in oxygen reduction reactions and as catalysts and/or mediators for the oxidation of hydrogen, alcohols or biomass in fuel cells [31–34]. The results obtained in [35] indicate the possibility of using a mixture of heteropoly compounds as a cathodic redox mediator in a hybrid fuel cell.

By using phosphomolybdic acid as an anodic mediator, Ding et al. [31] carried out a two-step process involving biofuel production and electricity generation from lignocellulosic biomass. This acid was also used as a mediator for biomass oxidation in combination with hydrogen evolution at the cathode, and it was shown that replacing anodic oxygen evolution with biomass oxidation using

**Table 1. Application of example HPCs in corrosion protection****Tabela 1. Zastosowanie przykładowych HPZ w ochronie przed korozją**

HPC	Protected metallic material	Mechanism of action of HPC	Corrosive environment	Literature reference
$H_6PMo_9V_3O_{40}$ $H_6PW_9V_3O_{40}$	S235 low carbon steel	cathodic inhibitor	0.5 M $H_2SO_4$	[10]
$H_6PMo_9V_3O_{40}$ $H_6PW_9V_3O_{40}$	S304 austenitic steel	anodic-cathode inhibitor	0.5 M $H_2SO_4$	[10]
$H_3PW_{12}O_{40}$ $H_4SiW_{12}O_{40}$	aluminium	reduction of the corrosion rate, shift of the breakdown potential towards positive potentials	hot water (90–300°C)	[7]
$(nC_7H_{15})_4N_5[PW_{11}O_{39}Cu(H_2O)]$	302 stainless steel	anodic-cathode inhibitor	0.25–1 M $H_2SO_4$	[21]
$SbW_9-TM-SnR$ $BiW_9-TM-SnR$ , where: TM = Mn, Co, Ni i Zn, SnR = Sn(CH <sub>2</sub> CH <sub>2</sub> COO)	20 carbon steel	anodic-cathode inhibitor	0.5–2 M HCl	[22]
$Na_3PW_{12}O_{40}$	carbon steel	anodic-cathode inhibitor	55% LiBr + 0.07 M LiOH	[23]
$H_3PMo_{12}O_{40}$ $H_3SiMo_{12}O_{40}$ as components of the PEDOT/ PyBA polymer matrix	X20Cr13 stainless steel	formation of insoluble deposits and passivation of the substrate, blocking by polyanions of the access of $Cl^-$ ions to the stainless steel surface	acidified sulphate solutions containing 0.5 M chloride ions	[24] [25]
$H_6PMo_{11}AlO_{40}$ $H_5PMo_{11}Al_{0.5}V_{0.5}O_{40}$	Al5052, Al7475, Al6062 aluminium alloys	no positive anti-corrosion effect, only $H_6PMo_{11}AlO_{40}$ showed a reduction in the corrosion rate and hydrogen evolution in the Al5052 alloy	2 M KOH	[27]

$H_3PMo_{12}O_{40}$  leads to a significant reduction in energy consumption in the hydrogen production process [32].

Heteropolyacids and their salts have also been used as electrolytes in electrochemical capacitors [36–38]. Due to the low electron conductivity of HPCs and their good solubility in most solvents, they were encapsulated in matrices of organometallic structures, immobilised on high surface area carbon substrates or in conducting polymer matrices to make them suitable for use as an active electrode material in supercapacitors [39, 40].

A wide range of Keggin-type HPAs have been tested for their ability to improve the electrocatalytic properties of Pt in the oxygen reduction reaction [41]. It has been shown that HPAs can be readily adsorbed onto Pt and activated carbon substrates to form electroactive adsorbates. When used in methanol fuel cells (MFCs), they increase the electrocatalytic activity of Pt in the methanol oxidation and oxygen reduction reactions and reduce the level of carbon monoxide contamination of the platinum catalyst [1, 42, 43]. As shown in studies [44–46], HPAs and their derivatives provide a wide range of possibilities in terms of the design and fabrication of highly efficient and stable precious metal-free electrocatalysts for both hydrogen evolution and oxygen reduction reactions.

Keggin-type HPAs are potential candidates for use in electrochemical devices such as fuel cells, electrolyzers, electrochemical capacitors or redox flow batteries (Table 2). The reversible multi-electron electrochemical activity of HPA has been documented in acidic aqueous media. However, there have not been sufficient studies focusing on the electrocatalytic activity of heteropolyacids in alkaline fuel cells, nickel-hydride cells and alkaline electrolyzers. Results presented in [41] show that  $H_3PMo_{12}O_{40}$  and  $H_3PW_{12}O_{40}$  exhibit poor redox activity in alkaline media. HPAs are degraded by concentrated bases with the formation of simple acids, which limits their practical application. Even though Xie

et al. [47] obtained electrochemically reduced polyoxometalates that are stable in alkaline solutions and, in combination with palladium, show excellent electrocatalytic activity for oxygen reduction reactions, further research development is needed to design new catalysts based on heteropoly compounds showing catalytic activity also for water-hydrogen reduction and oxidation reactions.

#### 3.4. Evaluation of the applicability of Keggin-type HPA in the preparation of hydride cells

ReNi<sub>5</sub>-type metallic materials (where Re is a rare-earth metal) can be used in the development of safe hydrogen storage systems and in nickel-metal hydride (Ni-MH) batteries. In order to meet the requirements for this type of material (significant rate of absorption/desorption of large amounts of hydrogen, as well as high corrosion resistance), their physicochemical properties can be shaped by modifying their chemical composition, structure or surface. The formation of catalytic HPC surface layers on hydrogen-absorbing alloys is an opportunity to significantly improve the kinetics of the electrode process of water reduction reaction to hydrogen and its oxidation.

One of the more important properties of heteropoly compounds that makes them useful in the fabrication of electrocatalytic composite materials is their ability to react reversibly to reduce transition metals and form mixed-valence forms [48]. Heterogeneous catalysts produced by HPA adsorption onto porous carbon materials [49], as well as metal oxides [50] and by incorporation into organometallic structures [51] offer certain advantages over homogeneous catalysts, such as stability, recoverability and reuse of the catalyst utilised. As shown in [52], electro-deposition of nickel from different heteropolyacid baths significantly improves the catalytic activity of nickel for hydrogen evolution reactions in acidic media.

It is known that pH influences the molecular structure of HPAs and thus the catalytic activity and is a determining factor in the

**Table 2. Examples of applications of Keggin-type HPAs in electrochemical energy conversion and storage devices**  
**Tabela 2. Przykładowe zastosowania HPK typu Keggina w urządzeniach do elektrochemicznej konwersji i magazynowania energii**

Heteropolyacids	Application	Literature reference
$H_3PW_{12}O_{40}$ $H_6CoW_{12}O_{40}$	negative and positive electrolyte and active material in redox flow batteries	[29] [30]
$H_3PW_{12}O_{40}$ $H_4SiW_{12}O_{40}$	electrolyte for electrochemical capacitors	[37] [38]
$H_3PMo_{10}V_2O_{40}$	supercapacitor composite electrode material	[40]
$H_3PMo_{12}O_{40}$ $H_4PMo_{11}VO_{40}$	anode mediator in the biomass oxidation reaction in a fuel bio-cell	[31]
$H_3PMo_{12}O_{40}$	catalyst and anode mediator in the hydrogen evolution reaction in modified PEM-type electrolyzers	[32] [33]
$H_3PMo_{12}O_{40}$ $H_5PV_2Mo_{10}O_{40}$ $H_6PV_3Mo_9O_{40}$	cathodic mediator in the oxygen reduction reaction in a polymer fuel cell	[34]
$H_3PMo_{12}O_{40}$ $H_3PW_{12}O_{40}$	in combination with Pt, a catalyst for the electro-oxidation of methanol in a methanol fuel cell	[42]
$H_3PMo_{12}O_{40}$ $H_3PW_{12}O_{40}$	oxygen evolution reaction catalyst in photoelectrochemical water splitting devices	[46]

performance of the redox process. The results presented in [53] showed that Keggin-type HPAs exhibit poor redox activity and low stability when tested in aqueous alkaline solutions. However, when immobilised on the surface of the carrier, they retain the Keggin structure even in strongly alkaline solution [54].

Heteropoly compounds, which improve the kinetics of electrode reactions, can provide an alternative to expensive catalysts such as platinum or palladium. In order to improve the efficiency of use and reduce the cost of precious metal-based catalysts, the authors of the paper [55] proposed a method involving the anchoring of Pt clusters on a support consisting of  $H_3SiW_{12}O_{40}$ -soot. This catalyst shows both good stability and high activity for the hydrogen evolution reaction. The results presented in [52] indicate that the nickel electrode modified with  $PW_{12}O_{40}^{3-}$  ions, in acidic media, is more electroactive than platinum and less sensitive than platinum.

HPAs are strongly adsorbed on metallic surfaces, which is of interest for anti-corrosion layers. The results presented in [24] indicate that negatively charged phosphomolybdic acid polyanions block the access of negative chloride ions to the stainless steel surface. The interaction of  $PMo_{12}O_{40}^{3-}$  with chromium(III), as well as iron(III) or iron(II), can lead to the formation of insoluble precipitates and display a general protective effect.

Passivation of  $ReNi_5$ -type materials in alkaline environments and the formation of bonds between passive layer components ( $La^{3+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$  ions, etc.) and HPA anions (e.g.  $PMo_{12}O_{40}^{3-}$ ,  $PW_{12}O_{40}^{3-}$ ,  $SiMo_{12}O_{40}^{4-}$  or  $SiW_{12}O_{40}^{4-}$ ) may provide an opportunity to create a protective barrier for the hydrophobic alloy against degradation during repeated hydrogenation/dehydrogenation cycles. The inhibitory properties of Mo- and W-containing anions are well documented [7], which would suggest that such layers could also play an additional protective role by inhibiting the dissolution processes of substrates typically containing >30 wt% lanthanum or other rare earth metals in their composition.

Due to the characteristics of heteropoly compounds, such as their ability to undergo rapid and reversible redox reactions, as well as their anti-corrosion activity, they could prove very appeal-

ing when it comes to the preparation of negative electrodes for Ni-MH batteries.

Preliminary results from our studies [54, 56, 57] indicate that phosphomolybdic acid immobilised on the surface of conductive C45 carbon black is stable in 6 M KOH solution and shows electrocatalytic properties. The presence of the  $C45-PMo_{12}O_{40}^{3-}$  carbon black nanocomposite in the powder mass of the hydride electrode catalyses the hydrogen evolution process and its oxidation reactions. Optimisation of the deposition conditions of different HPCs on carbon black C45 or the use of a different carrier can be expected to improve the performance for hydrogen absorption/desorption reactions in cyclic hydride electrode charge/discharge processes in a strongly alkaline environment.

#### 4. Conclusion

Heteropolyacids can be used in a wide range of processes, particularly in catalysis. One important feature of HPAs is that their composition can be modified by introducing different cations into their structures, allowing HPCs to be designed to catalyse specific reactions. Heteropolyacids show relatively low toxicity, reduce without major changes in their structure and exhibit anticorrosive activity. Furthermore, they are promising candidates for use in electrochemical energy conversion and storage devices, i.e. supercapacitors, fuel cells, and redox flow batteries. The reversible multi-electron electrochemical activity of heteropolyacids has been documented in acidic aqueous media. However, we do not have sufficient studies focusing on the electrocatalytic activity of heteropolyacids in alkaline environments. HPAs degrade in alkaline solutions with the formation of simple acids which limits their practical application. Therefore, a suitable method is required to modify/protect them from alkalis when used as electrocatalysts.

The development of simple, fast and convenient methods to immobilise polyoxometalates on the surface of hydride electrodes still remains a challenge. A detailed analysis of the literature predicts that surface modification of hydride materials with selected

heteropolyacids should reduce the hydrogen release overpotential, improve the kinetics of the electron transfer reaction at the electrode/electrolyte interface, and contribute to improving the operating durability of Ni-MH batteries.

#### Acknowledgements

This work was financially supported by the Ministry of Science and Higher Education of the Republic of Poland: BS/BP-200-301/2024 (KIM).

#### CRedit authorship contribution statement

**Krystyna Giza:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing.

**Karolina Kijańska:** Conceptualization, Data curation, Formal analysis, Methodology, Validation, Visualization, Writing – original draft.

### BIBLIOGRAPHY

- [1] M. Kourasi, R. G. A. Wills, A. A. Shah, F. C. Walsh. 2014. "Heteropolyacids for Fuel Cell Applications." *Electrochimica Acta* 127: 454–466. DOI: 10.1016/j.electacta.2014.02.006.
- [2] N. L. Z. Z. Adil, T. S. T. Saharuddin, L. N. Ozair, F. W. Harun. 2021. "Short Review on Heteropoly Acid Based Catalyst for Valorization of Biomass Waste into Valueable Chemicals." *IOP Conference Series: Materials Science and Engineering* 1173: 012073. DOI: 10.1088/1757-899x/1173/1/012073.
- [3] A. M. Escobar, G. Blustein, R. Luque, G. P. Romanelli. 2021. "Recent Applications of Heteropolyacids and Related Compounds in Heterocycle Synthesis. Contributions between 2010 and 2020." *Catalysts* 11(2): 291. DOI: 10.3390/catal11020291.
- [4] I. V. Kozhevnikov. 1998. "Catalysis by Heteropoly Acids and Multicomponent Polyoxometalates in Liquid-Phase Reactions." *Chemical Reviews* 98(1): 171–198. DOI: 10.1021/cr960400y.
- [5] N. Mizuno, M. Misono. 1997. "Heteropolyacid Catalysts." *Current Opinion in Solid State and Materials Science* 2(1): 84–89. DOI: 10.1016/s1359-0286(97)80109-x.
- [6] F. M. B. Gusmão, D. Mladenović, K. Radinović, D. M. F. Santos, B. Šljukić. 2022. "Polyoxometalates as Electrocatalysts for Electrochemical Energy Conversion and Storage." *Energies* 15(23): 9021. DOI: 10.3390/en15239021.
- [7] D. E. Katsoulis. 1998. "A Survey of Applications of Polyoxometalates." *Chemical Reviews* 98(1): 359–388. DOI: 10.101/cr960398a.
- [8] D. Cheng, K. Li, H. Zang, J. Chen. 2023. "Recent Advances on Polyoxometalate-Based Ion-Conducting Electrolytes for Energy-Related Devices." *Energy and Environmental Materials* 6: 6e12341. DOI: 10.1002/eem.212341.
- [9] P. Niemiec. 2021. "The Electronic Structure of Phosphotungstic ( $H_3PW_{12}O_{40}$ ) Heteropolyacids Modified by  $Fe^{2+}$  Cation." *Science, Technology and Innovation* 11(4): 24–32. DOI: 10.5604/01.3001.0014.7530.
- [10] G. E. Badea, A. Fodor, A. I. G. Petrehele, I. Maior, M. Toderas, C. M. Morgovan. 2023. "Evaluation of Phosphopolyoxometalates with Mixed Addenda (Mo, W, V) as Corrosion Inhibitors for Steels." *Materials* 16(24): 7600. DOI: 10.3390/ma16247600.
- [11] H. Kim, P. Kim, J. Yi, K. Y. Lee, S. H. Yeom, I. K. Song. 2006. "Preparation and Catalytic Activity of  $H_3PMo_{12}O_{40}$  Catalyst Molecularly Immobilized on Polystyrene Support." *Studies in Surface Science and Catalysis* 159: 297–300. DOI: 10.1016/s0167-2991(06)81592-2.
- [12] M. Rękas. 2024. *Ogniwa paliwowe. Wykład VI*. [https://home.agh.edu.pl/~radecka/doc/Ogniwa\\_SOFC.pdf](https://home.agh.edu.pl/~radecka/doc/Ogniwa_SOFC.pdf) (access: 19.02.2024).
- [13] J. J. Zhu, R. Benages-Vilau, P. Gomez-Romero. 2020. "Can Polyoxometalates Enhance the Capacitance and Energy Density of Activated Carbon in Organic Electrolyte Supercapacitors?" *Electrochimica Acta* 362: 137007. DOI: 10.1016/j.electacta.2020.137007.
- [14] M. Genovese, K. Lian. 2017. "Polyoxometalate Modified Pine Cone Biochar Carbon for Supercapacitor Electrodes." *Journal of Materials Chemistry A* 5: 3939–3947. DOI: 10.1039/C6TA10382K.
- [15] P. E. Phyu Win, J. X. Wang, X. Y. Jia, B. Qi, W. Chena, L. He, Y.-F. Song. 2020. "Synergistic Effects of Polyoxometalate with  $MoS_2$  Sheets on Multi-Walled Carbon Nanotubes Backbone for High-Performance Supercapacitor." *Journal of Alloys and Compounds* 844: 156194. DOI: 10.1016/j.jallcom.2020.156194.
- [16] H. Li, W. Qi, H. Sun, P. Li, Y. Yang, L. Wu. 2008. "A Novel Polymerizable Pigment Based on Surfactant-Encapsulated Polyoxometalates and Their Application in Polymer Coloration." *Dyes and Pigments* 79(2): 105–110. DOI: 10.1016/j.dyepig.2007.11.008.
- [17] R. Li, Y. Wang, F. Zeng, C. Si, D. Zhang, W. Xu, J. Shi. 2023. "Advances in Polyoxometalates as Electron Mediators for Photocatalytic Dye Degradation." *International Journal of Molecular Sciences* 24(20): 15244. DOI: 10.3390/ijms242015244.
- [18] S. Herrmann, L. De Matteis, J. M. de la Fuente, S. G. Mitchell, C. Streb. 2017. "Removal of Multiple Contaminants from Water by Polyoxometalate Supported Ionic Liquid Phases (POM-SILPs)." *Angewandte Chemie International Edition* 56(6): 1667–1670. DOI: 10.1002/anie.201611072.
- [19] T. Fotiou, T. M. Triantis, T. Kaloudis, E. Papaconstantinou, A. Hiskia. 2014. "Photocatalytic Degradation of Water Taste and Odour Compounds in the Presence of Polyoxometalates and  $TiO_2$ : Intermediates and Degradation Pathways." *Journal of Photochemistry and Photobiology A: Chemistry* 286: 1–9. DOI: 10.1016/j.jphotochem.2014.04.013.
- [20] A. Al-Dawsari, A. M. Turkustani, F. Bannani. 2019. "Acid-Resistant Corrosion Protection Polyoxometalate Ionic Liquids as Anticorrosion Coatings." *Journal of Materials and Environmental Sciences* 10(11): 1135–1151.
- [21] A. Misra, I. F. Castillo, D. P. Müller, C. González, S. Eyssautier-Chuine. 2018. "Polyoxometalate-Ionic Liquids (POM-ILs) as Anticorrosion and Antibacterial Coatings for Natural Stones." *Angewandte Chemie International Edition* 57(45): 14926–14931. DOI: 10.1002/anie.201809893.
- [22] X.-F. Wang, X.-Y. Liu, F. Su, J.-S. Li, Z.-M. Zhu, X.-J. Sang, L.-C. Zhang. 2022. "Enhanced Corrosion Resistance of Carbon Steel in Hydrochloric Acid Solution by Polyoxometalate-Esterin Derivatives." *ACS Omega* 7(5): 4429–4443. DOI: 10.1021/acsomega.1c06276.
- [23] X. Q. Hu, C. H. Liang, X. N. Wu. 2011. "Corrosion Behaviors of Carbon Steel in 55% LiBr Solution Containing PWVA Inhibitor." *Materials and Corrosion* 62: 444–448. DOI: 10.1002/maco.200905528.
- [24] L. Adamczyk, P. J. Kulesza. 2011. "Fabrication of Composite Coatings of 4-(Pyrrole-1-Yl) Benzoate-Modified Poly-3,4-Ethylenedioxythiophene with Phosphomolybdate and Their Application in Corrosion Protection." *Electrochimica Acta* 56(10): 3649–3655. DOI: 10.1016/j.electacta.2010.12.078.
- [25] L. Adamczyk, K. Giza, A. Dudek. 2014. "Electrochemical Preparation of Composite Coatings of 3,4-Ethylenedioxythiophene (EDOT) and 4-(Pyrrole-1-Yl) Benzoic Acid (PyBA) with Heteropolyanions." *Materials Chemistry and Physics* 144(3): 418–424. DOI: 10.1016/j.matchemphys.2014.01.012.
- [26] J. Hou, G. Zhu, J. Zheng. 2011. "Synthesis, Characterization and Corrosion Protection Study of Polypyrrole/Phosphotungstate Coating on Low Alloy Steel in Seawater." *Polymer Science Series B* 53: 546. DOI: 10.1134/S1560090411100034.
- [27] A. P. Atencio, J. R. Aviles, D. Bolaños, R. Urcuyo, M. L. Montero, D. González-Flores, P. Ocoñ. 2022. "Anti-Corrosive Additives for Alkaline Electrolyte in Al-Air Batteries:  $NH_4VO_3$  and Polyoxometalates." *Electrochemical Science Advances* 2(4): e2100125. DOI: 10.1002/elsa.202100125.
- [28] V. S. Korenev, T. S. Sukhikh, M. N. Sokolov. 2023. "A Series of Lanthanide Complexes with Keggin-Type Monolacunary Phosphotungstate: Synthesis and Structural Characterization." *Inorganics* 11(8): 327. DOI: 10.3390/inorganics11080327.
- [29] T. Feng, H. Wang, Y. Liu, J. Zhang, Y. Xiang, S. Lu. 2019. "A Redox Flow Battery with High Capacity Retention Using 12-Phosphotungstic Acid/Iodine Mixed Solution as Electrolytes." *Journal of Power Sources* 436: 226831. DOI: 10.1016/j.jpowsour.2019.226831.

- [30] Y. Y. Liu, S. F. Lu, H. N. Wang, C. M. Yang, X. Su, Y. Xiang. 2017. "An Aqueous Redox Flow Battery with a Tungsten–Cobalt Heteropolyacid as the Electrolyte for Both the Anode and Cathode." *Advanced Energy Materials* 7(8): 1601224. DOI: 10.1002/aenm.201601224.
- [31] Y. Ding, B. Du, X. Zhao, J. Y. Zhu, D. Liu. 2017. "Phosphomolybdic Acid and Ferric Iron as Efficient Electron Mediators for Coupling Biomass Pretreatment to Produce Bioethanol and Electricity Generation from Wheat Straw." *Bioresource Technology* 228: 279–289. DOI: 10.1016/j.biortech.2016.12.109.
- [32] X. Du, W. Liu, Z. Zhang, A. Mulyadi, A. Brittain, J. Gong, Y. Deng. 2017. "Low-Energy Catalytic Electrolysis for Simultaneous Hydrogen Evolution and Lignin Depolymerization." *Chemistry–Sustainability–Energy–Materials* 10(5): 847–854. DOI: 10.1002/cssc.201601685.
- [33] C. W. Anson, S. S. Stahl. 2020. "Mediated Fuel Cells: Soluble Redox Mediators and Their Applications to Electrochemical Reduction of O<sub>2</sub>, and Oxidation of H<sub>2</sub>, Alcohols, Biomass, and Complex Fuels." *Chemical Reviews* 120(8): 3749–3786. DOI: 10.1021/acs.chemrev.9b00717.
- [34] T. Matsui, E. Morikawa, S. Nakada, T. Okanishi, H. Muroyama, Y. Hirao, T. Takahashi, K. Eguchi. 2016. "Polymer Electrolyte Fuel Cells Employing Heteropolyacids as Redox Mediators for Oxygen Reduction Reactions: Pt-Free Cathode Systems." *ACS Applied Materials and Interfaces* 8(28): 18119–18125. DOI: 10.1021/acsami.6b05202.
- [35] L. Z. Abunaeva, E. A. Ruban, M. A. Myachina, P. A. Loktionov, D. E. Verakso, A. A. Pustovalova, M. M. Petrov, D. V. Konev, N. N. Gavrilova, A. E. Antipov. 2022. "A Mixture of Phospho-, Vanadium-, and Molybdo-Heteropolyacids as a Promising Cathode Redox-Mediator for Hybrid Hydrogen–Air Fuel Cells." *Russian Journal of Electrochemistry* 58: 938–945. DOI: 10.1134/s1023193522100032.
- [36] H. Gao, K. Lian. 2011. "Proton Conducting Heteropoly Acid Based Electrolyte for High Rate Solid Electrochemical Capacitors." *Journal of The Electrochemical Society* 158: A1371–A1378. DOI: 10.1149/2.064112jes.
- [37] M. Skunik-Nuckowska, S. Dyjak, K. Grzejszczyk, N. H. Wisińska, F. Béguin, P. J. Kulesza. 2018. "Capacitance Characteristics of Carbon-Based Electrochemical Capacitors Exposed to Heteropolytungstic Acid Electrolyte." *Electrochimica Acta* 282: 533–543. DOI: 10.1016/j.electacta.2018.06.070.
- [38] K. Lian, C. Li. 2008. "Heteropoly Acid Electrolytes for Double-Layer Capacitors and Pseudocapacitors." *Electrochemical and Solid-State Letters* 11(9): A158–A162. DOI: 10.1149/1.2955861.
- [39] A. A. Vannathan, P. R. Chandewar, D. Shee, S. S. Mal. 2022. "Asymmetric Polyoxometalate-Polypyrrole Composite Electrode Material for Electrochemical Energy Storage Supercapacitors." *Journal of Electroanalytical Chemistry* 904: 115856. DOI: 10.1016/j.jelechem.2021.115856.
- [40] A. M. Mohamed, M. Ramadan, N. Ahmed, A. O. A. ElNaga, H. H. Alalawy, T. Zaki, S. A. Shaban, H. B. Hassan, N. K. Allam. 2020. "Metal–Organic Frameworks Encapsulated with Vanadium-Substituted Heteropoly Acid for Highly Stable Asymmetric Supercapacitors." *Journal of Energy Storage* 28: 101292. DOI: 10.1016/j.est.2020.101292.
- [41] A. S. Cherevan, S. P. Nandan, I. Roger, R. Liu, C. Streb, D. Eder. 2020. "Polyoxometalates on Functional Substrates: Concepts, Synergies, and Future Perspective." *Advanced Science* 7(8): 1903511–1903534. DOI: 10.1002/advs.201903511.
- [42] J. R. Ferrell, M.-C. Kuo, J. A. Turner, A. M. Herring. 2008. "The Use of the Heteropoly Acids, H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> and H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, for the Enhanced Electrochemical Oxidation of Methanol for Direct Methanol Fuel Cells." *Electrochimica Acta* 53(14): 4927–4933. DOI: 10.1016/j.electacta.2008.01.102.
- [43] R. Włodarczyk, M. Chojak, K. Miecznikowski, A. Kolary, P. J. Kulesza, R. Marassi. 2006. "Electroreduction of Oxygen at Polyoxometalate-Modified Glassy Carbon-Supported Pt Nanoparticles." *Journal of Power Sources* 159(2): 802–809. DOI: 10.1016/j.jpowsour.2005.11.061.
- [44] Z. Zeb, Y. Huang, L. Chen, W. Zhou, M. Liao, Y. Jiang, H. Li, L. Wang, L. Wang, H. Wang, T. Wei, D. Zang, Z. Fan, Y. Wei. 2023. "Comprehensive Overview of Polyoxometalates for Electrocatalytic Hydrogen Evolution Reaction." *Coordination Chemistry Reviews* 482: 215058. DOI: 10.1016/j.ccr.2023.215058.
- [45] Z.-H. Wang, X.-F. Wang, Z. Tan, X.-Z. Song. 2021. "Polyoxometalate/Metal–Organic Framework Hybrids and Their Derivatives for Hydrogen and Oxygen Evolution Electrocatalysis." *Materials Today Energy* 19: 100618. DOI: 10.1016/j.mtener.2020.100618.
- [46] M. Sarnowska, K. Bieńkowski, P. J. Barczuk, R. Solarska, J. Augustyński. 2016. "Highly Efficient and Stable Solar Water Splitting at (Na)WO<sub>3</sub> Photoanodes in Acidic Electrolyte Assisted by Non-Noble Metal Oxygen Evolution Catalyst." *Advanced Energy Materials* 6(14): 1600526. DOI: 10.1002/aenm.201600526.
- [47] X. Xie, Y. Nie, S. Chen, W. Ding, X. Qi, L. Li, Z. Wei. 2015. "A Catalyst Superior to Carbon-Supported-Platinum for Promotion of the Oxygen Reduction Reaction: Reduced-Polyoxometalate Supported Palladium." *Journal of Materials Chemistry A* 3(26): 13962–13969. DOI: 10.1039/c5ta02196k.
- [48] Q. Li, L. Zhang, J. Dai, H. Tang, Q. Li, H. Xue, H. Pang. 2018. "Polyoxometalate-Based Materials for Advanced Electrochemical Energy Conversion and Storage." *Chemical Engineering Journal* 351: 441–461. DOI: 10.1016/j.cej.2018.06.074.
- [49] A. A. Ensafi, E. Heydari-Soureshjani, M. Jafari-Asl, B. Rezaei. 2016. "Polyoxometalate-Decorated Graphene Nanosheets and Carbon Nanotubes, Powerful Electrocatalysts for Hydrogen Evolution Reaction." *Carbon* 99: 398–406. DOI: 10.1016/j.carbon.2015.12.045.
- [50] A. Saccà, A. Carbone, R. Pedicini, M. Marrony, R. Barrera, M. Elomaa, E. Passalacqua. 2008. "Phosphotungstic Acid Supported on a Nanopowdered ZrO<sub>2</sub> as a Filler in Nafion-Based Membranes for Polymer Electrolyte Fuel Cells." *Fuel Cells* 8(3–4): 225–235. DOI: 10.1002/uce.200800009.
- [51] W. Ali Shah, S. Ibrahim, S. Abbas, L. Naureen, M. Batool, M. Imran, M. Arif Nadeem. 2021. "Nickel Containing Polyoxometalates Incorporated in Two Different Metal–Organic Frameworks for Hydrogen Evolution Reaction." *Journal of Environmental Chemical Engineering* 9(5): 106004. DOI: 10.1016/j.jece.2021.106004.
- [52] O. Savadogo, D. L. Piron. 1990. "New Hydrogen Cathodes in Acid Medium: Case of Nickel Electrodeposited with Heteropolyacids (HPAs)." *International Journal of Hydrogen Energy* 15(10): 715–721. DOI: 10.1016/0360-3199(90)90002-G.
- [53] M. Kourasi. 2015. *Heteropolyacids and Non-Carbon Electrode Materials for Fuel Cell and Battery Applications*. Doctoral thesis. University of Southampton, Engineering and the Environment.
- [54] K. Giza. 2022. "Electrochemical Characterization of C45 Carbon Black-H<sub>3</sub>P-Mo<sub>12</sub>O<sub>40</sub>-Polyvinylidene Fluoride System." *Ochrona przed Korozją* 65(11): 340–343. DOI: 10.15199/10.2022.11.1.
- [55] T. Zhang, S. Weng, X. Wang, Z. Zhang, Y. Gao, T. Lin, Y. Zhu, W. Zhang, C. Sun. 2022. "Platinum Atomic Clusters Embedded in Polyoxometalates-Carbon Black as an Efficient and Durable Catalyst for Hydrogen Evolution Reaction." *Journal of Colloid and Interface Science* 624: 704–712. DOI: 10.1016/j.jcis.2022.06.018.
- [56] K. Giza. 2019. "Communication – A New Catalytic Application of H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> in the Performance of Hydride Electrode for Ni-MH Battery." *Journal of The Electrochemical Society* 166: A3332–A3334. DOI: 10.1149/2.0751914jes.
- [57] K. Giza, E. Owczarek, A. Miszczyk. 2023. "The Effect of C45 Carbon Black-Phosphomolybdic Acid Nanocomposite on Hydrogenation and Corrosion Resistance of La<sub>2</sub>Ni<sub>9</sub>Co Hydrogen Storage Alloy." *Energies* 16(10): 4002. DOI: 10.3390/en16104002.