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Review

Polyoxometalate-based materials for advanced electrochemical energy conversion and storage

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HIGHLIGHTS

- The electrochemical energy conversion and storage about POMs have been discussed.
- The structure properties of POMs has been summarized.
- The applications include redox flow batteries, fuel cells, Na/Li-ion batteries.
- With the increasing of POM structures, this chemistry shows exciting prospects.

GRAPHICAL ABSTRACT

POMs-based materials and their composite nanomaterials comprehensively summarized and evaluations are given in this review.

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ABSTRACT

Electrochemical energy storage plays a significant role in solving the issues of energy shortage and environmental pollution. Recently, polyoxometalates (POMs) have received significant attention as promising materials for electrodes in electrochemical energy conversion and storage devices. To improve electrochemical performance, POMs can be modified by a variety of techniques and methods. Their open frameworks, consisting of independent structural units that possess potential catalytic properties, can meet the requirements of cutting-edge technologies and demonstrate advantages over routine insertion-type open frameworks with limited one-electron transfer properties or conversion materials with compact ligand linkage. Here, a class of electrochemically stable cluster-like POMs are discussed for applications as open framework electrodes. In this paper, the latest research progress on POMs-based materials is introduced, and current applications in advanced electrochemical energy conversion and storage are highlighted; these applications include Li- and Na-ion batteries, redox flow batteries, and fuel cells.

1. Introduction

Over the last decade, scientists and politicians around the world have recognized the urgent need for sustainable energy conversion and storage to solve the problems of environmental pollution and energy shortage. To this end, researchers have been working to improve the performance of electrochemical devices. Functional compounds are required to act as electrode materials in order to convert solar energy or electrical energy into stored energy [1–4]. Among these materials, composites based on POMs have received significant attention in the field of energy storage in recent years [5–8]. POMs are anionic molecular metal oxides based on high-valent transition metals (e.g., V, Mo,

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W), which possess great potential to meet the demands of cutting-edge technologies [9–13]. The open frameworks consist of independent structural units, which possess potential for catalytic activity, that can meet these demands with advantages over routine insertion-type open frameworks that have limited one-electron transfer properties or conversion materials with compact ligand linkage [14–19]. However, its electronic conductivity from molecular metal-oxostructure is low and furthermore its anion is prone to dissolve in electrolyte [20–23]. POMs are usually activated by coordination to conductive materials. Therefore, POMs-based materials have been investigated because they can significantly modify the electronic structure of the clusters, consequently, equipment performance in batteries [5,20,24–26]. According to recent research progress into the chemical modification of POMs, these new materials show large surface areas and good electrical conductivity [27–30]. The investigation of POMs-based materials is an important area, with a large number of POMs crystal structures reported in the literature. As a consequence, researchers have begun to exploit the synergistic effects of POMs-based materials [31–33].

This review summarizes the recent applications of POMs-based materials in advanced electrochemical energy conversion and storage, including Li- and Na-ion batteries, redox flow batteries and fuel cells. Furthermore, the crystal structures, synthetic methods, and electrochemical performances of POMs-based materials are systematically presented. The outlook section focuses on viewpoints of the authors on the future perspectives in the field, which is inspired by recent landmark results or by concepts that have yet to be fully realized (Table 1).

2. Structures and physicochemical properties of POMs

POMs are groups of inorganic, anionic, nanometersized (around 1 nm) metal oxide clusters, exhibiting substantial variety in charge and framework structures. POMs are transition metal oxide clusters that are composed of transition metals in their highest oxidation states. They can be presented by the general formula: $[M_mO_y]^{n-}$ for isopolyanions and $[X_xM_mO_y]^{n-}$ for heteropolyanions, where X is a hetero atom, usually a main group element (P, Si, Ge, As), and M is an addenda atom, usually a d-block element with high oxidation state (V^{V}, Mo^{VI} or W^{VI}) [34].

POMs are always negatively charged, and the negative density depends mainly on the elemental composition and the molecular structure. Generally, POMs consist of three or more transition metal oxyanions with shared oxygen atoms, forming a large closed three-dimensional framework [35,36]. The metal atoms that make up the framework are called addenda atoms, usually group V or VI transition metals (such as V, Nb, Ta, Mo, W, etc.) in high oxidation states. One or more heteroatoms (such as P, Si, Ge, etc.) are enclosed in the center of the framework; these heteroatoms share adjacent oxygen atoms with transition metal ions [37,38].

Table 1
The POMs-based materials for Li- and Na-ion batteries.

Sample	Electrode	Specific capacity [$mA\,h\,g^{-1}$]	Rate [C or $mA\,g^{-1}$]	Cycle number	Refs.
$Li_7[V_{15}O_{36}(CO_3)]$	Cathode	140	10	100	[71]
$K_7NiV_{13}O_{38}$	Cathode	200	17	24	[74]
NAM/acetylene black	Cathode	437	0.04	50	[149]
SWNTs/Py-SiW_{11}	Anode	580	0.5	100	[89]
CNTs-SiW_{11}	Anode	650	0.5	100	[105]
TBA-$PMo_{11}V$/CNTs	Anode	850	0.5	100	[106]
SiW_{12}/rGO	Cathode	275	50	–	[117]
AgNPs/POMs	Anode	1760	0.1	50	[126]
Mo_6-SCN	Anode	1678	50	100	[137]
$Na_2H_8[MnV_{13}O_{38}]$/G	Cathode	190	0.1	100	[150]
$Na_6[V_{10}O_{28}]\cdot16H_2O$	Anode	276	20	25	[151]

$Na_3[AlMo_6O_{24}H_6]$-(NAM); single-walled carbon nanotubes-(SWNTs); $(Bu_4N)_4\{(SiW_{11}O_{39})\ [O(SiCH_2CH_2CH_2NHCOOCH_2C_{16}H_9)_2]\}$-(Py-$SiW_{11}$); $TBA_4[PMo_{11}VO_{40}]$-(TBA-$PMo_{11}V$); $H_4SiW_{12}O_{40}$-(SiW_{12}); silver nanoparticles (AgNPs); $[(Bu_4N)_2[Mo_6O_{18}$-*N*-Ph-(*o*-$CH_3)_2$-*p*-SCN]-(Mo_6-SCN).

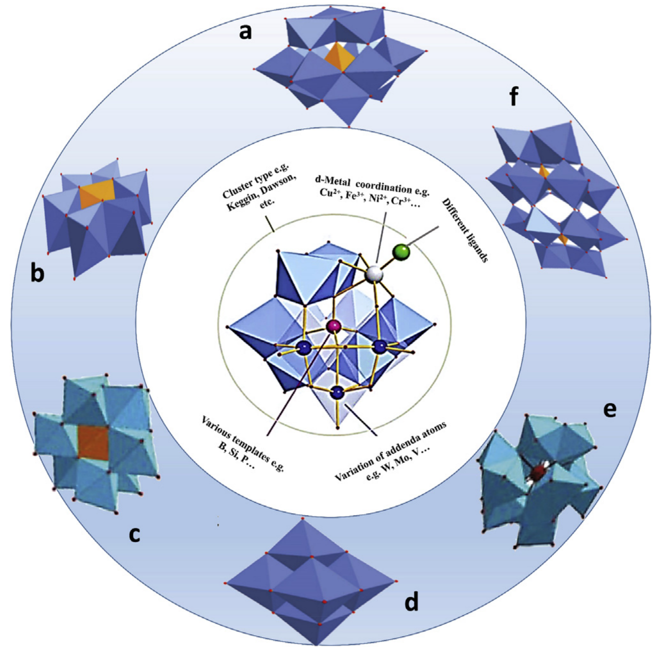

Fig. 1. Six typical structures of polyoxometalates: (a) Kegin, (b) Anderson, (c) Waugh, (d) Lindqvist, (e) Silverton, (f) Dawson. (c, e) Reproduced with permission [39]. Copyright 2016, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (a,b,d,f) Reproduced with permission [18]. Copyright 2015, The Royal Society of Chemistry 2015.

Following the development of POMs chemistry, several types of structures have been found. The most representative and important compounds in this family are shown in Fig. 1, which depicts six fundamental POMs structures: (a) Kegin, (b) Anderson, (c) Waugh, (d) Lindqvist, (e) Silverton, and (f) Dawson [40]. These structures can be distinguished by the ratio of the addenda atoms to the hetero atoms as follows: Keggin and Silverton structures have a 1:12 ratio, Dawson and Waugh have a 1:9 ratio, and Anderson has a 1:6 ratio and Lindqvist has a 6:19 ratio. The most common route is the hydrolytic removal of one or more metal sites from (typically W based) Keggin or Dawson anions, resulting in so-called lacunary species (such as $[SiW_{12}O_{40}]^{4-} \rightarrow [SiW_{11}O_{39}]^{8-}$ + "WO^{4+}"), in which empty binding sites are available for further functionalization with the addition of new metal ions [41].

POMs can undergo metal and valence ion exchange; these derivatives not only increase the overall structural range of POMs, but they also improve their practical application [25]. Due to the versatility of these structures, POMs present a wealth of characteristics. The main physicochemical properties of POMs are as follows: 1) good thermal stabilities, large molecular sizes, and relatively high molecular weights (10^3–10^4); 2) highly concentrated, non-toxic, tasteless, non-volatile, and soluble in oxygenated organic solvents such as water, ether, ethanol, acetone, etc.; 3) superior redox properties. Most POMs can be reduced to blue, which is called the "heteropoly blue", and oxidation can restore the color [42]. By adjusting the structure and composition of POMs, the redox potential can be easily adjusted [43]; the last property involves being 4) easily modified by surfactants to effectively prevent POMs from polymerizing and obtaining various organic/inorganic hybrid materials [43,44].

Thus, due to the increase number of publications on POMs-based batteries, it is necessary to systematically summarize the advances in this field and introduce further trends. The number of papers on POMs-based materials published in recent years are illustrated according to the Science Citation Index (Fig. 2).

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