Engineering Materials

Ram K. Gupta *Editor*

Metal Phosphates and Phosphonates

Fundamental to Advanced Emerging Applications

Springer

Engineering Materials

This series provides topical information on innovative, structural and functional materials and composites with applications in optical, electrical, mechanical, civil, aeronautical, medical, bio- and nano-engineering. The individual volumes are complete, comprehensive monographs covering the structure, properties, manufacturing process and applications of these materials. This multidisciplinary series is devoted to professionals, students and all those interested in the latest developments in the Materials Science field, that look for a carefully selected collection of high quality review articles on their respective field of expertise.

Indexed at Compendex (2021) and Scopus (2022)

Ram K. Gupta
Editor

Metal Phosphates and Phosphonates

Fundamental to Advanced Emerging Applications

Springer

Editor
Ram K. Gupta
Department of Chemistry
Pittsburg State University
Pittsburg, PA, USA

ISSN 1612-1317 ISSN 1868-1212 (electronic)
Engineering Materials
ISBN 978-3-031-27061-1 ISBN 978-3-031-27062-8 (eBook)
https://doi.org/10.1007/978-3-031-27062-8

© The Editor(s) (if applicable) and The Author(s), under exclusive license to Springer Nature Switzerland AG 2023
This work is subject to copyright. All rights are solely and exclusively licensed by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.
The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.
The publisher, the authors, and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, expressed or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This Springer imprint is published by the registered company Springer Nature Switzerland AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Contents

An Introduction

Sunil Kumar Baburao Mane, Naghma Shaishta, G. Manjunatha, and Asif Hayat

Abstract The type of inorganic-organic hybrid polymeric material formed by the coordination of phosphonate ligands to metal ions, resulting in multi-dimensional extended assemblies is metal phosphonates (MPs). The discipline of MPs chemistry has developed progressively over the last few decades, fueled by interest in applications in a wide range of fields. Synthetic technologies of MPs are lacking on the way to domestic, more efficient alternatives. For the characterization, the advancement of electron diffraction as an instrument for crystal structure determination and the use of in situ characterization techniques have allowed for a better understanding of reaction pathways. Metal phosphonates have been discovered to be appropriate materials for a wide range of applications. This chapter continues to concentrate on advanced emerging applications of MPs in bio-ceramics, electrochemical energy devices, fuel cells, state-of-the-art hydrogen evolution rate (HER), oxygen evolution rate (OER), and water splitting catalysts. The remaining eighteen chapters in the book demonstrate the vast expansion and diversity of metal phosphonate chemistry research briefly.

Keywords Metal phosphate and phosphonates · Water splitting catalysts · Electrochemical energy devices · Fuel cells

---

S. K. B. Mane · N. Shaishta (✉)
Department of Chemistry, Khaja Bandanawaz University, Kalaburagi, Karnataka 585104, India
e-mail: nghmachem@gmail.com

G. Manjunatha
Department of Chemistry, Shri Siddhartha Institute of Technology, Tumkur, Karnataka 572101, India

A. Hayat (✉)
State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350002, P. R. China
e-mail: asifncp11@yahoo.co

R. K. Gupta (ed.), *Metal Phosphates and Phosphonates*, Engineering Materials,
https://doi.org/10.1007/978-3-031-27062-8_1

1 Introduction

The goal of this chapter is to compile important and contemporary research publications on the intriguing chemistry of metal phosphate and phosphonates. Metal phosphates (MPs) are a large group of structurally adaptable acidic solids that perform exceptionally well in a variety of applications such as catalysts, fuel cells, batteries, biomedical devices, and so on. These P-containing synchronization primitives can be synthesized using a variety of methods which are frequently simple to access, providing a relatively vast array of key components. Reliant on metal phosphate mixtures and synthetic techniques, MP solids can be generated in a wide range of crystalline shapes, from 1D polymeric structures to layered networks to 3D open frameworks [1]. These solids' benefits include being inexpensive and simple to prepare, being hydrophilic and thermally stable, and having some structural design ability. Their structures can also be altered after syntheses, such as by adding ionic or neutral species that have a big impact on their functionality and other crucial characteristics, like the development of hydrogen bonding networks [2]. The main group, alkaline, transition, and rare-earth metals can be combined with these ligands to create strong, nanocrystals that can be used in a wide range of processes, including electrostatic interaction, gas adsorption, molecular recognition, catalysis, and reinforcement for therapeutic systems [3]. Such materials have an ancient legacy that started in the 1970s with the autonomous groundbreaking studies done by Giulio Alberti and Abraham Clearfield.

Relying on phenyl phosphonic acid, Alberti published the discovery of the inaugural multilayer Zr phosphonate in 1978 [4]. Clearfield subsequently discovered the crystal structure of this compound in 1993 [5]. This Zr-modified version revealed a brand-new chemistry premised upon the efficient artificial material scheme owning custom-made characteristics as a result of the synergistic participation of both the metal type and organic component of the linkers. It is regarded as the quintessential framework of all metal phosphonates.

Past developments have seen the publication of many thorough assessments of this subject [6]. But, the in-depth study of novel ligands with varying degrees of complexity and utility propelled this chemistry in unanticipated directions and to thrilling breakthroughs in the realm of the development of novel nanomaterials. The First European Workshop on Metal Phosphonate, which took place in Swansea (UK) in September 2018, gathered the most recent aids from many subject-matter specialists, and this chapter compiles them. The workshop was a one-day gathering that was planned to provide the top researchers in the area of MPs chemistry with a place for debate. The seminar's invited speakers addressed a wide range of subjects, including new synthetic techniques, porous materials, catalysis, batteries, and tissue engineering. The collaborative viewpoint paper titled "New Directions in Metal Phosphonate and Phosphinate Chemistry" [7] compiles a thorough summary of the workshop. This viewpoint enumerated potential fresh ideas for research study and summarized all of the writers' workshop presentations. Due to the First European Workshop on Metal Phosphonate Chemistry's success, a second one has been

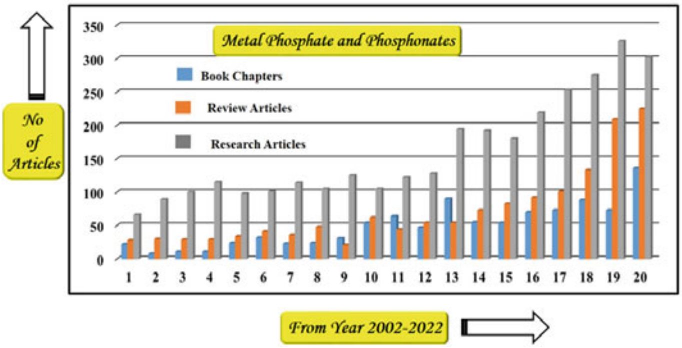

Fig. 1 The number of publications with entitled metal phosphate and phosphonates from Science Direct (2002–2022)

planned for Berlin (Germany Federal)'s Institute for Materials Research and Testing (BAM) on September 24, 2019.

Figure 1 shows the two-decade (2002–2022) data of many publications with entitled metal phosphate and phosphonates from Science Direct, which shows the advancement of research work going on in this field. This chapter begins by going back in time and recounting a couple of the most significant phases of historical research with a particular emphasis on architectural chemistry because the field of MPs has advanced significantly. The methodologies for fabrication and characterization are covered in the following section, with a focus on cutting-edge techniques like rising production for the creation of novel substances, mechano-chemical synthesis, techniques for creating porous architectures, framework remedy from the diffraction pattern, and in situ analytical techniques. The next segment concentrates on innovative MP applications, such as medication administration, electrochemical devices, catalysis, and gas sorption/separation. Lastly, we consider what the field's prospective new may include while attempting to pinpoint the much more potential fresh lines of inquiry.

2 Ancient Point of View

The research from Clearfield et al. in the area of tetravalent metal phosphates was recognized for strong ion exchange capabilities since the 1950s and sparked initial interest in the field. In 1968, Clearfield used single-crystal X-ray diffraction (SCXRD) data to determine the crystal structure of -zirconium bis(monohydrogen orthophosphate) monohydrate [$Zr(HPO_4)_2 \cdot H_2O$, referred to as -ZrP] [8]. The layered assembly of α-ZrP is made up of Zr atoms that are tridentate monohydrogen phosphate subunits that are octahedrally linked, allowing free hydroxy groups that face toward the interlayer space and form hydrogen bonds with the molecules of water fitted between the sheets. An extensive study was conducted to take benefit of the acidic hydrogen on the exterior of the layers, particularly for ion exchange and complexation reasons, as a result of the atomic level comprehension of the construction of α-ZrP. An arena of MPs was introduced in 1978 [4] by Alberti and Costantino et al. Three zirconium phosphonates were created: zirconium ethylphosphate ($Zr(C_2H_5OPO_3)_2$), zirconium phenyl phosphonate ($(Zr(C_6H_5PO_3)_2$, and zirconium hydroxymethyl phosphonate ($Zr(HOCH_2PO_3)_2$). They were unable to find acceptable single crystals for use in the SCXRD to solve the structures because of the extremely high poor solubility of these substances.

The researchers speculated that these substances might well produce a similar network structure to α-ZrP because of their comparable synthesis procedure and focused primarily on powder X-ray diffraction (PXRD) patterns ruled by intense basal peaks at low angles. In α-ZrP, the hydroxyl groups in the interlayer are replaced by the organic substituent, which decides the interlayer distance. In the years that followed, several comparable substances were created using both mono and di phosphonates to produce comparable stacked or walled layer structures. The first MP derivatives have been based on tetravalent metals, particularly zirconium, but in the late 1970s and 1980s, numerous frameworks premised on divalent metal ions have been developed. Cunningham et al. [9] conducted preliminary research and reported an easy synthetic procedure on divalent metal phenyl phosphonate and phenylarsonates, $M(C_6H_5PO_3)$ and $M(C_6H_5AsO_3)$ [M^{2+} = Mg, Mn Fe, Co, Ni, Cu, Zn, and Cd] by a simple reaction with the chloride or sulfate metal salts. Appreciation to the inferior solubility of these materials, associated with tetravalent MPs, single crystals might be developed.

A variety of important articles documenting the crystal assemblies of numerous divalent MPs appeared toward the conclusion of the 1980s. Each of these substances had layers formed by connecting metal atoms and phosphonate groups, with the organic substituent residing in the interlayer space. One of the instances given by Cao et al., where a variety of structures based on divalent metals remained published, relying on SCXRD measurements, encompassed: Mn, Mg, Ca, Cd, and Zn and explained the layered crystal structure of $Mn(C_6H_5PO_3)\cdot H_2O$ [10]. Beginning in the 1990s, MPs structures spread out across the entire periodic table, including all of the lanthanide series, a variety of transition metals, and more than half of the alkali and alkaline earth elements. Major advances had also been achieved in resolving the crystal structures using PXRD observations during this development over the periodic table. This one was crucial for the area MPs because it has frequently been challenging to create an appropriate single crystal for SCXRD, particularly when using metals having high oxidation levels. A case in point is the groundbreaking research of Alberti and Costantino et al. who've been unsuccessful in obtaining massive crystals of $Zr(C_6H_5PO_3)_2$. Poojary et al. finally resolved the framework from PXRD statistics in 1993 [5] using a mixture of optimization techniques, Patterson strategies, and Rietveld processes, proving that Alberti and Costantino et al. 15-year-old's expectation was accurate and that the structure of Zr phenyl phosphonate was predicated on the identical layered setup of -ZrP.

The advent of more potent crystallographic programs, better accessible radiation accelerators, and the production of more advanced laboratory powder X-ray diffractometers have all contributed to the design approaches from PXRD becoming a powerhouse for scientists dealing with MPs. Although the vast number of MPs identified in the first 15 decades of studies had layered architectures, some open framework MPs were discovered in the early to mid-1990s. The earliest instances were all built on the tiny ligand methyl phosphonic acid, which, when mixed with Cu, Zn, and Al, produced frameworks with a broadcast organization that was evocative of several zeolite structures. Further research in this area was encouraged by the structural resemblance to zeolites which were at the time the most significant class of crystalline and microporous materials. As a result, further principles set substances were discovered, the majority of which were built on mono phosphonates or di phosphonates having short alkyl chains. In virtually all cases, lengthening the alkyl chains led to the formation of multilayered architectures, prohibiting the enlargement of the channel width and the production of more porous materials [7].

Three methods were developed to stop the enlargement of the structure from growing to combat the high tendency of MPs to polymerize: Incorporating sterically demanding moieties onto the framework of phosphonic acids, utilizing terminal auxiliary ligands that really can fill coordination sites on the metal ions, employing premade clusters, and conducting regulated ligand interchange are all examples of this [11]. The researcher can consult the book "Metal Phosphonate Chemistry: from Synthesis to Applications" which also has a chapter on the early history of MPs chemistry, written by Abraham Clearfield [12] if they are eager for a more thorough overview of the development of the field up to 2011.

3 Synthesis of Metal Phosphate and Phosphonates

The various synthetic route for the production of metal phosphate and phosphonates were represented in Fig. 2.

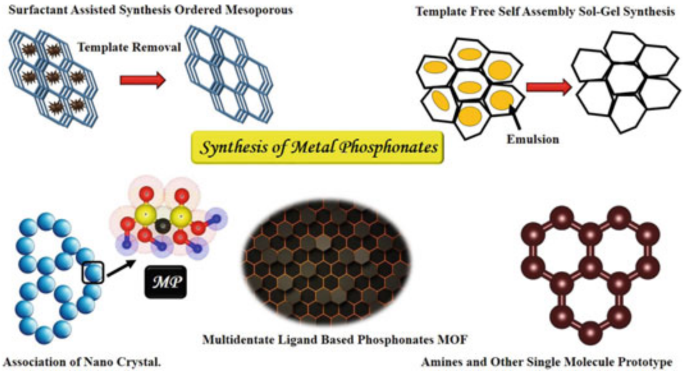

Fig. 2 Various synthetic routes for metal phosphate and phosphonates

3.1 Micro Porous Metal Phosphate

Numerous research activities were undertaken for the designing of metal phosphates via hydrothermal technique after the finding of microporous alumino-phosphonates using amino-centered organic molecules which possess 2D and 3D construction assembly. As a result, over time, a diverse set of outline configurations, as well as isomorphous replacement by responsive catalytic metal atoms, have emerged. With the help of various organic pattern fragments, microporous aluminophosphates made of substitute alumina and phosphate tetrahedrons with impartial outline structures are disclosed with a wide variety of pore sizes. As models, a variety of primary, secondary, and tertiary amines, quaternary ammonium cations, alcohols, and so on are used to create these microporous materials. Later on, a hypothetical example constructed on host-guest communications to elucidate the outline nanostructures of microporous materials using solvo or hydrothermal processes was proposed. In addition to the standard pathways, the ionothermal process, in which an ionic liquid can be used as both a solvent and a model, was shown to be valuable for its structure-directing character in constructing these metal phosphate-based nano-architectures. These porous nanostructures can be created using the microwave-assisted heating technique, which significantly reduces the time needed for crystallization and the entire synthetic process to just an insufficient minute.

Microwave production frequently results in minor constituent parts using greater morphological regularity while maintaining crystallinity in aluminum phosphates. The resultant materials have important adsorption and catalytic capabilities and can comprise a huge amount of 3d transition elements and also non-transition elements [13]. Owing to the mixture of the Lewis acidity and redox characteristics of these transition metals in heterogeneous catalysis, their isomorphous substitution in $AlPO_4$ networks is frequently highly advantageous. Due to their great chemical constancy and extensive potential for adjusting the superficial acidity to meet the requirements for an anticipated catalytic response, these silico alumino phosphates have drawn specific consideration to isomorphous replacement of Al or P by Si in the corresponding $AlPO_4$ outlines [14]. The embedding of organic assemblies at the pore superficial can add elasticity, performance, and hydrophobicity to the subsequent organic-inorganic hybrid resources in addition to the integration of the inorganic substituent in these phosphate-built constituents. In this regard, a phenyl-functionalized large pore alumino phosphate resource using phenyl phosphoric acid as the phosphate source has been reported [15].

Owing to the large toughness, phenyl assemblies can be additionally functionalized with responsive organic clusters to complete the anticipated request potential. Constructing metallo phosphate molecular filters requires a careful fundamental route, which is facilitated by models. The pH of the production units for these phosphate-based microporous resources is reserved slightly acidic, in contrast to the manifestation of high silica zeolites, which frequently includes tetra alkyl ammonium cations. Maximum amines protonate in slightly acidic circumstances and can cooperate electrostatically with phosphate anions to steady the formation of the operational distinct components, which serve as nucleating types in guiding the crystal structures. In this area, work has been effective in creating microporous phosphate-based resources with an AFI outline and globular constituent part morphologies using tiny biomolecules as structure guiding representatives, such as tetramethylguanidine. It has also been reported that crystalline microporous aluminophosphate and metallo alumino phosphate resources have been developed using the Ni(II) complex as a prototype [16]. Here, the size of the relevant multifaceted and the kind of nonbonding purposeful assemblies are important structural factors that influence the development of porous structures.

When crystallization is in process, in situ XRD and spectroscopic analyses of the manufactured gel frequently shed light on the crystallization process and the function of substrates in these preparations. To determine the crystallization methodology of Co-APO-5, Weckhuysen and colleagues examined the time-resolved SAXS/WAXS and spectroscopic investigations [17]. Their study revealed the organization of predominant amorphous metal and phosphate concrete members, followed by accelerated evaporation to linear Al-O-P groups in the proximity of template molecules, and eventually quick restructuring to establish the porous crystalline structure. Some of the most common synthetic approaches for manufacturing microporous and mesoporous metal phosphates and phosphonates were sol-gel and ligand-assisted solvothermal synthetic processes, as well as hydrothermal methods, are among them.

3.2 Mesoporous Metal Phosphates

The complex molecular surfactant arrangement aided material production by the morality of charge transfer among both zirconium sulfate polyanions and the cationic surfactant in the synthesis of ordered mesoporous zirconium oxophosphate material has been well published.

A large well-organized surface area of mesoporous titanium phosphates with cationic and anionic surfactant molecules self-assembling as structure guiding mediators was nicely synthesized. Ti(IV) positions may perhaps engage with anionic surfactants, however anionic phosphate possibly will connect with a cationic surfactant to maintain the well-arranged mesophases in organic molecules. In the corresponding synthetic routes, charged Ti(II) sites and negatively charged phosphate sites could interact with each other to form new molecules.

By using self-assembly with cetyltrimethylammonium bromide (CTAB) as a template underneath hydrothermal circumstances, scientists were able to create mesoporous cobalt phosphate with episodic nanostructures and crystalline pore walls [18]. This mesoporous material's highly precise superficial area, crystalline pore wall, and plenty of catalytic spots significantly aid in its electrocatalytic movement in the oxygen evolution reaction. The wormhole-based designed mesoporous phosphate titania in the company of Pluronic P123, where almost even pore channels of dimensions are arbitrarily organized to form a 3D structure has been testified [19].

Furthermore, the robust P-O-Ti attachment in this mesoporous phosphate titania encourages supplementary cross-linking of the surface imperfection spots to steady the mesostructure. With the help of UV/visible light irradiation, the vast surface region structured with tetrahedral Ti(IV) centers maintains its catalytic function in the degradation of n-pentane. Zhao et al. have tuned the ordered mesophase of titanium phosphate from 2D-hexagonal to cubic, and then into the lamellar nanostructure in this context by varying the surfactant (P123)/(Ti+P) molar ratio [20].

Here, the creation of stably ordered mesophases was substantially guided by the links among the acid-base pairs of the metals and phosphate. Triblock copolymer supramolecular construction is repeatedly detected to be an extremely helpful framework for the production of spherical nanoparticles of materials depending on aluminum organo phosphonate (AOP) and aluminum phosphate. In contrast hand, Liu et al. created an AlPO polymer using a hydrothermal synthesis gel that contained a tiny organic molecule called citric acid that might engage with the aluminophosphate matrix during the nucleation and polycondensation stages and produce consistent mesopores [21].

3.3 Mechanochemical Synthesis

Mechanochemistry has a lengthy history dating back more than a thousand years but has only subsequently gained popularity as a practical technique in chemical processing. Since the past 20 years, there has been a massive campaign for environmentally friendly and renewable chemistry, which may be one of the chief factors why mechanochemistry has since attracted much increasing emphasis in a variety of useful sectors. The general idea is evident, although there is still a variety of specifics to be worked up regarding the precise mechanisms that underlie mechanochemical production.

The interaction among two or more solids to create the quality output is commonly driven by the supply of mechanical power, i.e., through crushing or milling, and frequently occurs with minimal or no solvent. Mechanochemistry is more interesting in part because processes can go forward through routes that aren't available by traditional techniques [7]. The cadmium-based Mps $Cd(O_3PPh)\cdot H_2O$ and $Cd(HO_3PPh)_2$ were obtained via a vibration ball milling process when cadmium acetate dehydrate and phenyl phosphonic acid was shared inside a reaction container in several ratios (1:1, 1:2, and 1:4) and then milled for 15 min along with stainless steel balls [22]. Because water and acetic acid were released during the reaction, causing all of the compounds acquired through milling to be moist, this indicates that every step of the production was actually helped by liquids. Further investigation towards replacing cadmium with Mn, Co, and Ni was done $M(HO_3PPh)_2(H_2O_3PPh)_2(H_2O)_2$ MPs in the same year [23]. Following 15 min of smooth crushing, the scientists succeeded in synthesizing three pure chemicals using the outlined method. For each of the components, researchers also conducted a liquid-assisted grinding (LAG) run, and they discovered that it had no impact on the results acquired relative to the dry course. The researchers realized that such a method may be used to quickly and simply synthesize different molecular MPs. Because of the flexibility, minimal influence on the environment, rapidity of production, and additionally, the potential for commercial uses exists.

4 Applications

With particular emphasis on the recent 20 years (from 2002–2022) of advances, this chapter covers the current state of the art in drug delivery, proton conductive or fuel cell, electrochemical water splitting, and bio-ceramaic applications of metal phosphates. Figures 3 and 4 shows a summary of publishing patterns which includes book chapter, review, and research articles taken from the science direct collection, which attests to the rising popularity of this subject over time.

4.1 Medication Transport Implementation

For the creation of ionic-strength pharmaceutical delivery systems, the bidirectional protonation-deprotonation of the oxidative stress activity in permeable nanoarchitectures is very essential. By jointly employing mono- and bis-phosphonic acid functionalities like organophosphorus substrates, together with built-in L-proline and piperazine functions for such colon-focused ionic strength discharge of DNA

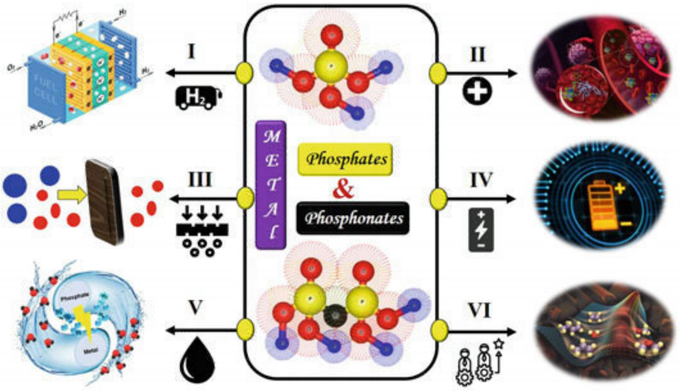

Fig. 3 Numerous applications of metal phosphate and phosphonates. Where, I: metal phosphonated MOF (fuel cells), II: biomaterial (drug transport and bioceramics), III: membrane (ion exchange and gas sorption), IV: energy storage (battery and supercapacitors), V: photocatalysis and electrochemical cells (water splitting, HER, OER and CO_2 reduction and VI: catalysts of synthesis (biofuel and petrochemical)

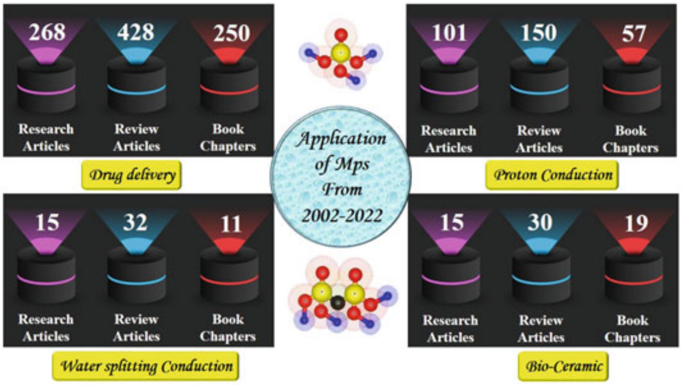

Fig. 4 Statistical data from Science Direct (2002–2022) on Metal phosphate and phosphonates in various fields

molecules, a report disclosed highly porous zirconium phosphonates. The main benefits of using phosphonate functionalized porous polymers as pharmaceutical logistics companies also include their minimal cytotoxicity rate and good biocompatibility. To create covalent imine group-based organic nanostructured resources, research has been undertaken to functionalize cellulose nanocrystals with (bis) phosphonate, which encompasses alendronate and 3-aminopropyl phosphoric acid.

Phosphonates substituents in such components seem to be especially beneficial in the prevention of bone density, and they can also be connected to fluorophores to deliver effective therapeutic agents for bone biosensing. Supramolecular nano valves, for instance, predicated on the synthesis process of phosphonated column arteries over mesoporous silica nanoparticles (MSNs), could indeed perform extremely proficiently as just a vehicle for drug delivery [24]. The phosphonate groups in the MSNs regulate the discharge of prescription medications for tumor photothermal chemotherapy by ion-pairing with quaternary ammonium ions in the nanostructure. Guest molecules frequently prevent the mesopores of these MSNs, preventing the stimuli-responsive intercellular delivery of medications on supply. Rim et al. demonstrated that coating the pore exterior of MSNs with the environmentally benign biological material calcium phosphate could perhaps perform extremely proficiently as just an ionic strength pore inhibition for the continuous flow of apprehended therapeutic agents [25]. Underneath slightly acid pH circumstances, intracellular partitions which include lysosomes and endosomes might discharge the encapsulated active ingredients kept inside the porous structure.

Covalent bonding using phosphonate assemblies allows biopolymer-like chitosan to somehow be successfully deposited over functionalized MSNs, which in turn causes the painkiller ibuprofen to discharge in a pH-responsive manner. Via scientific investigations, it had been discovered that fructose 1,6-bisphosphate can be employed as a phosphonate linkage representative for the production of a blended highly porous strontium-loaded calcium phosphate nanomaterial. This material serves as an effective drug-delivery motor for antibiotic drugs such as vancomycin and significantly improves the skeletal capacity when combined with collagen.

For the manufacture of highly porous hydroxyapatite, a sodium hexa metaphosphate as a phosphate precursor had been employed to transport the pH-responsive anticancer medication doxorubicin (Dox). Zhang et al. have created a mixed nanomaterial for the loading of the anticancer medication Dox that has covalently linked highly porous calcium phosphate nanoparticles with a cylindrical enclosure nanostructure and contains photoresponsive components encapsulating polydopamine [26]. In medical research, chemo-photo thermal treatment and improved cinematography are both simultaneously provided by this hybrid nano-architectured polymer.

4.2 Electrode Materials/Proton Conduction for Fuel Cells

For the production of numerous divalent and trivalent metal phosphates, the existence of organic molecules as charge-compensating ions was required, whereas tetravalent and monovalent metal phosphates are typically prepared by orthodox synthetic methods [27]. For a high intrinsic proton conduction process, the metal phosphate must contain an acidic group namely $H_2PO_4^-$ and $H_2PO_4^{2-}$. Furthermore, a particular chemical alteration or influenced morphological alterations, such as the creation of nanoplatelets or nanorods particles, might result in extrinsic proton conduction, related to associated epidermal proton transportation. As both proton transporters as well as in the creation of H-bonding connections within the structure, water molecules play a role.

Additionally, several techniques, like intercalation and post-synthesis adsorption, may be used to incorporate additional foreign entities, like organic components, into their architecture. Consequently, the hydrophilic system boundaries and water/guest molecule interactions play a unique role in MP hydrogen transportation [28]. As a result, the proton-transfer process in metal phosphates like CsH_2PO_4 or $CaHPO_4 \cdot 2H_2O$ [29] includes both the free rotation of the phosphate groups and the H^+ jump. Other times, the proton-transfer process behaves incorrectly, as it does in the instance of KH_2PO_4 [30]. A “proton jump” or the Grotthuss mechanism, both of which have a lower ionization potential, are frequently used to describe proton transportation within a quasi-liquid state [29]. Identifying proton propagation pathways is crucial to creating proton conductor materials. Therefore, proton-containing opposing charges such as hydronium ions, NH_4^+, protonated amine groups, as well as protonated organic compounds in particular ought to be included in the framework when an automotive process is required. It can also be necessary to immobilize particular functional groups and their accompanying counter ions onto the architecture.

However, materials that show proton transportation via a Grotthuss-type mechanism primarily have persistent H-bond systems which encourage H^+ conduction having low activation energy (Ea). The latter substances' fundamental flaw is that, at a specific temperature, the H-bond systems may rupture, releasing water molecules in the process, necessitating the development of persistent H-bonding systems containing hydrophilic pathways or the investigation of another suitable conductive medium [31]. The advancement of fuel cells in relation to energy production, environmental concerns, as well as the steady degradation of traditional energy reserves is a research subject of utmost importance. Perfluorinated sulfonic acid (PFSA) ionomers, including Nafion® as well as Aquivion®, are frequently utilized in PEMFCs and DMFCs as polymer electrolyte vesicles (PEM) for working temperatures below 120 °C from the numerous sort of solid electrolytes that are created in the last numerous centuries [32]. Improved conductivity characteristics, varying between 9×10^{-3} and 1.2×10^{-1} S/cm, as well as mechanical and chemical durability, are to blame for this [33].

Nafion® does, though, have a few significant disadvantages, including methanol absorption, increased price, complicated processing method, operating under 100 °C to retain the hydration of the membrane, as well as additional problems with catalyst performance. Because of everything said above, advanced membrane substances must be developed [34]. The utilization of low-loading expensive metal catalysts is made possible by intermediate temperature fuel cells (ITFCs) that run from 120 to 300 °C and avoid certain of these issues. They also accomplish lower catalyst toxicity and improved management of the hydration parameters. However, potential electrolyte breakdown must be researched mostly in terms of methanol HT-PEMFCs, which must run over 250 °C and under elevated pressure [35]. Throughout this book chapter, we update significant innovations in super protonic and tetravalent metal phosphate/pyrophosphate proton conductors. The creation of new proton carrier systems that depend on divalent and trivalent metal phosphates is also updated, as well as their development and design.

To build an effective power source that uses H_2 (fuel) and O_2 molecules to produce electrical energy, it's indeed extremely desirable to develop a porous membrane that exchanges protons with substantial proton conductivity [36]. In this regard, a ternary nanocomposite membrane composed of branched-chain triphosphonic acid NMPA, sulfonated polysulfone, and titania has been described [37]. This nanocomposite membrane had a proton conductivity of 0.002 S/cm at 150 °C, making it perfect for use in fuel cells. Since the labile protons of the free phosphate groups can move between different acid sites via their pore channels, porous nanoarchitecture built on phosphates and phosphonates are considered necessary in this aspect. A phosphonic acid-functionalized mesoporous silica was produced using CTAB-assisted hydrothermal co-condensation of different percentages of diethyl phosphate, ethyltriethoxy silane, and tetraethoxysilane [38].

For the fabrication of a multilayer Co–Ca bimetallic MOF, Zheng et al. used a bridging tetraphosphonic acid–based ligand, and it demonstrated a significant shift in the proton conductivity across various humidity levels [39]. Investigating their viability as a sensing element requires a significant shift in the proton conductivity with humidity. 5-(phosphonomethyl)isophthalic acid was employed by Wei et al. [40] as a ligand in the production of a Eu-based MOF with a multilayer anionic framework structure. Proton transportation is made easier by the hydrogen-bonded links that are formed along the pore axis by this Eu-MOF carrying surface phosphonate groups. The zirconium phosphonate-based material $Zr(O_3P\text{-}OH)(O_3PC_6H_4SO_3H)$ was created by Alberti et al. using phosphoric acid and meta sulfophenylene phosphonic acid as the phosphate origin, and it displayed an incredibly high proton conductivity of 0.1 S/cm at a reasonably low temperature (100 °C) in 90% RH [41]. To comprehend the unrestricted passage of protons within the nanospheres in the phosphonate-based Ni-MOF, Schroder et al. have used quasielastic neutron scattering investigations [42]. Contrarily, Krautscheid et al. used solid-state MAS NMR spectroscopic investigations on a phosphonate-based La-MOF to determine the movement of molecules of water within the pore axis of the MOF with a pore size of 1.9 nm [43].

4.3 Electrochemistry of Water Splitting

Another active field of study from an energy and sustainability standpoint is the creation of noble-metal-free electrochemical accelerators for such process of hydrogen evolution reaction (HER) and the oxygen reduction reaction (ORR) or oxygen evolution reaction (OER) through the electrochemical separation of water. The metal complexes are frequently unsustainable in water electrolysis separation, although certain heterocyclic compounds of transition elements have strong initial reactivity. As a result, metal phosphonate-based hybrid nanostructures, which are significantly stable over a broader pH scale, may be extremely beneficial again for the redox process. IrO_2-based nanostructures perform well for OER, however, their expensive price is a key limitation for these catalysts. Pt NP-based nanomaterials are indeed the reference HER electrocatalysts. As a result, nonprecious metal-based catalytic systems, particularly those that use metal phosphates and phosphonates, can provide a significant benefit in this situation [28].

A study on a nanocomposite consisting of nano carbon and N-doped cobalt phosphate for well-organized ORR at alkaline pH is given in this background [44]. N-doping in graphitic carbon and Co–N interaction with cobalt phosphate were the two factors that contributed to the substantial ORR performance. Utilizing NMPA as little more than a phosphate precursor, F127 and polyvinyl alcohol as templates, work has been reported on a porous cobalt phosphonate exhibiting multilayered porosity with sizes of 1.5–5.0 micropore/mesopore and nanocages (20–60 nm). This cobalt phosphonate outline's large area of surface and nanoscale permeability was discovered toward being extremely advantageous because of its excellent electrochemical performance within the alkaline water oxidation process. The production of cobalt phosphonates ornamented N-doped carbon using a phosphonate-bridged MOF has additionally been done. Such material has been used as an accelerator for electrochemical water-splitting reactions [45].

It has been hypothesized that greater OER action is caused by deformed geometry at the metal centers and extended Co–O and Co–Co bond lengths based on XAS and XPS research. Pinna and colleagues have compiled many coordination polymers and MOFs based on metal phosphonates for creating metal phosphates, phosphides, and oxyhydroxides, and the end products demonstrated significant electrocatalytic activity in HER or OER [46]. Furthermore, a nanocomposite material that is made of cobalt phosphate NPs supported over nitrogen and phosphorus co-doped mesoporous carbon has been reported and a high HER (acidic pH) and OER (alkaline pH) are produced by such multi-component catalytic system, which effectively supports the overall water separation response [47]. Transition metal phosphate electrocatalysts are emerging as a potential for OER or ORR in water splitting or metal-air batteries since they are inexpensive with good electrochemical behavior.

Nevertheless, it remains difficult to find polyfunctional electrocatalysts with good electrochemical results for OER and ORR. In this perspective, for zinc-air batteries, Pan et al. have reported a simple self-template fabrication method for 2D amorphous N-doped CoFe-mesoporous phosphate micro sheets [48]. The ideal 2D amorphous N-doped CoFe-phosphate shows greater electrocatalytic activity for both OER and ORR, which displays an inferior overpotential of 313 mV at 10 mA/cm^2 for OER besides a high half-wave potential of 0.74 V for ORR. The Zn-air battery that this multifunctional electrocatalyst was used in also had a high power density (74.6 m W/cm^2), precise capacity (750 mAhgZn^{-1}), and long-lasting consistency (over 30 h at 10 mA/cm^2). Hence such research offered a fresh approach to synthesizing new 2D heteroatom-doped electrocatalytic components with mesoporous structures for power conversion purposes, particularly in rechargeable Zn-air batteries.

4.4 Bioceramics

In bioceramics, where inorganic materials are primarily employed to fix and replace damaged human skeletal system components, metal phosphates have a considerable opportunity. Highly permeable metallo phosphates are bioactive glasses that can be used to engraft both hard and soft tissues and to keep giving bones the necessary tenacity and stretchability. Calcium orthophosphate, which is frequently used as a biocompatible substance for bone, achilles tendon, and tooth replacement, in addition to skeletal tissue creation, is one of the crucial elements in this frame of reference [28]. The effective synthesis of calcium orthophosphate, commonly known as hydroxyapatite (HA), can indeed be accomplished by condensing calcium(II) salts with triethyl phosphite in a sol-gel process. As bone fillers, hybrid fiber-reinforced composites made of biodegradable polymers and HA-type bioceramics are frequently used because they may quickly create pore structures in bone formation and speed up the healing course. In this regard, Bernstein and colleagues explored bone tissue development by implanting micro porous beta-tricalcium phosphate [49] and it was found that by their physical adsorption, genuine tissue and good skeletons could be formed in 52 weeks.

Microspores were discovered to be extremely helpful for the regeneration of tissues including bone, muscle, and perhaps other vital organs in the 3D calcium phosphate nanostructure. When designing frameworks for bone and tissue regeneration, natural polymers are frequently combined alongside bioactive ceramics [50]. For the creation of Nano synthetic structures in biomedical applications, hierarchical permeability ranging from the nanoscale to macrospores is typically very advantageous. Such hybrids' polymers afford the required rigidity and flexibility, and their metallo phosphates offer them the strength properties that may be appropriate for human bone. Such artificial biomaterials' permeability may significantly support the development of connective tissues and keep the right amount of fluid inside the bones. Restorative dentistry procedures frequently employ metallic titanium discs.

It is easier for the skeletal components and the phosphonates mounted Ti prosthesis to communicate chemically when the implants are coated with phosphonic acids at their edges, which results in a much-enhanced interaction with bones. As a result, the crosslinking of phosphate can provide an ecologically friendly method for placing dental implants. For instance, poly(beta-amino ester)-based gels and cryogels with phosphonate functionalization are redox-responsive, exhibit low cytotoxicity, and are biodegradable when used in in vitro cell culture investigations. Consequently, there is a significant chance that these phosphonated materials will be investigated as tissue manufacturing platforms.

5 Standpoints and Obstacles for the Forthcoming

The successful synthesis of mesoporous silico alumino phosphate is one of the most difficult assignments to investigate in the coming years. The addition of regular mesopores in conjunction with a zeolite-like polycrystalline pore wall should bypass the transport restriction of porous structure materials and so make it an ideal contender in heterogeneous catalysis, despite studies on compounds with progressive meso-micro highly skewed permeability. Relative to microporous H-ZSM-5 and H-SAPO-5, hierarchically porous H-SAPO-5 did in fact exhibit improved catalytic performance for the benzene alkylation utilizing benzyl ethanol as an efficient catalyst. A strong Bronsted acidity can be achieved through pyridine-IR in mesoporous silicoalumino phosphate materials such as MESO-SAPO-5.

The enhanced catalytic efficiency again for the alkylation of phenol using propylene oxide is mostly attributable to the highly skewed permeability in this catalyst's solid acid structure. Because the production gel for each of these metallo phosphates- and phosphonate-based compounds contain metal ion progenitors, the utilization of tiny chelating agents like salicylic acid may act as a blueprint for creating the corresponding highly porous nanostructural design. By utilizing unusual framework compounds generated through biomass resources, like glucose, citric acid, or biopolymers including sodium alginate, inter crystallite meso porosity in the microporous materials can be established.

Sustainable development is among the key challenges in chemical studies. The production of such porosity nano-architectured compounds will undoubtedly be very efficient thanks to certain framing techniques utilizing biomaterials. The variety of the scaffolding formulations is one of the special benefits of metal phosphate- and phosphonate-based porous nanostructural design. Based on the choice of SDAs, a wide range of polyvalent metals can produce matching metal phosphates and phosphonates. By employing water-in-oil surfactant micelles with surfactant patterning for just a slow crystallization approach, work has been reported in which $CePO_4$ nanowires are made of linear or twisted strands with a consistent thickness of 3.7 nm. Extended production times could be controlled using preservatives or even microwave heating conditions to create nanomaterials with precisely defined particle shapes and porosities. Another significant area is chiral catalysis, where phosphonate-based homochiral porous materials have a lot of unrealized potential.

Hexa-connected Ni(II) containing bridging bi naphthyl bisphosphonate binders could be synthesized by a hydro or solvo thermal synthesis method to create 1D zigzag chain-like phosphonate-based MOFs. These phosphonate-based MOFs might function as an efficient catalyst for the enantioselective hydrogenation process due to the structural characterization of these kinds of low dimensional conjugated polymers that include pretty distorted octahedral Ni(II) centers. In light of their content, structure architecture, pore diameters, and simplicity of post-synthetic surface modification with reactive organic groups, one can examine the applicability of these porous nanomaterials. The viability of such components in different energy, environmental, and biological requests has now been expanded by the use of heterogeneous ligands in addition to phosphates to create chemically stable and mechanically resilient phosphonate-based MOFs. By having interstitial organic functional groups, highly porous phosphonates have the potential to create multi-constituent catalytic converters through post-synthetic functionalization and carbonization. Future research would only further enhance the chemical properties of such porous materials by identifying innovative nano infrastructures of metal phosphate- and phosphonate-based microporous and mesoporous components for catalysis, adsorption, photonics, electrochemical cells, battery storage, and biomedical applications

6 Conclusion

Nano structural design with very large areas of surface and nanoscale pores that vary in length from a few nanometers to 50 nm. The porous metal phosphate and phosphonates reported above-mentioned are composed of appropriate metals and phosphate/phosphonate-based ligands. Porous nanomaterials have found many practical applications in catalysis, gas storage/adsorption, optoelectronics, electrochemical cells, fuel cells, and medicinal fields thanks to their structural stability and diversity in compositional changes. Because diverse metal ions have substantial binding affinities for phosphate-based ligands, these nanostructures are extremely resistant to harsh chemical conditions. Additionally, by combining these metal phosphates and phosphonates with 2D nanostructures like reduced graphene oxide, graphitic carbon nitride, etc., they will significantly increase their conductivity and mobility of ions and electrons, increasing their potential for use in electrochemical and optoelectronic applications. Furthermore, the development of novel phosphonate-based fusions with photo-, pH-, or thermo-responsive functionalities may enhance their possibilities for use in many cutting-edge fields including energy, the environment, biomedical sciences, etc.

References

1. Shivhare, A., Kumara, A., Srivastava, R.: Metal phosphate catalysts to upgrade ligno-cellulose biomass into value-added chemicals and biofuels. Green Chem. **23**, 3818–3841 (2021)
2. Cheng, Q., Zhao, X., Yang, G., Mao, L., Liao, F., Chen, F., He, P., Pan, D., Chen, S.: Recent advances of metal phosphates-based electrodes for high-performance metal ion batteries. Energy Storage Mater. **41**, 842–882 (2021)
3. Taddei, M., Costantino, F.: Metal phosphonates and phosphinates. Crystals **9**, 454 (2019)
4. Alberti, G., Costantino, U., Allulli, S., Tomassini, N.: Crystalline $Zr(R\text{-}PO_3)_2$ and $Zr(R\text{-}OPO_3)_2$ compounds (R = organic radical). A new class of materials having layered structure of the zirconium phosphate type. J. Inorg. Nucl. Chem. **40**, 1113–1117 (1978)
5. Poojary, M.D., Hu, H.L., Campbell, F.L., Clearfield, A.: Determination of crystal structures from limited powder data sets: crystal structure of zirconium phenylphosphonate. Acta Crystallogr. Sect. B **49**, 996–1001 (1993)
6. Bao, S.S., Shimizu, G.K.H., Zheng, L.M.: Proton conductive metal phosphonate frameworks. Coord. Chem. Rev. **378**, 577–594 (2019)
7. Shearan, S.J., Stock, N., Emmerling, F., Demel, J., Wright, P.A., Demadis, K.D., Vassaki, M., Costantino, F., Vivani, R., Sallard, S., Salcedo, I.R., Cabeza, A., Taddei, M.: New directions in metal phosphonate and phosphinate chemistry. Curr. Comput. Aided Drug Des. **9**, 270 (2019)
8. Clearfield, A., David, S.G.: The crystallography and structure of α-zirconium bis(monohydrogen orthophosphate) monohydrate. Inorg. Chem. **8**, 431–436 (1969)
9. Cunningham, D., Hennelly, P.J.D., Deeney, T.: Divalent metal phenylphosphonates and phenylarsonates. Inorg. Chim. Acta. **37**, 95–102 (1979)
10. Cao, G., Lee, H., Lynch, V.M., Mallouk, T.E.: Synthesis and structural characterization of a homologous series of divalent-metal phosphonates, $MII(O_3PR)\cdot H_2O$ and $MII(HO_3PR)_2$. Inorg. Chem. **27**, 2781–2785 (1988)
11. Goura, J., Chandrasekhar, V.: Molecular metal phosphonates. Chem. Rev. **115**, 6854–6965 (2015)
12. Clearfield, A.: The Early History and Growth of Metal Phosphonate Chemistry. In Metal Phosphonate Chemistry, pp. 1–44. Royal Society of Chemistry, Cambridge, UK (2011)
13. Ristic, A., Tusar, N.N., Arcon, I., Logar, N.Z., Thibault-Starzyk, F., Czyzniewska, J., Kaucic, V.: Large-pore FAPO-36: synthesis and characterization. Chem. Mater. **15**, 3643–3649 (2003)
14. Martens, J.A., Grobet, P.J., Jacobs, P.A.: Catalytic activity and Si, Al, P ordering in microporous silicoaluminophosphates of the SAPO-5, SAPO-11, and SAPO-37 type. J. Catal. **126**, 299–305 (1990)
15. Yan, W., Hagaman, E.W., Dai, S.: Functionalization of aluminophosphate $AlPO_4$-H1 (VPI-5) with phenylphosphonic acid. Chem. Mater. **16**, 5182–5186 (2004)
16. Garcia, R., Shannon, I.J., Slawin, A.M.Z., Zhou, W., Cox, P.A., Wright, P.A.: Synthesis, structure and thermal transformations of aluminophosphates containing the nickel complex $[Ni\text{-}(Diethylenetriamine)_2]^{2+}$ as a structure directing agent. Micropor. Mesopor. Mater. **58**, 91–104 (2003)
17. Grandjean, D., Beale, A.M., Petukhov, A.V., Weckhuysen, B.M.: Unraveling the crystallization mechanism of CoAPO-5 molecular sieves under hydrothermal conditions. J. Am. Chem. Soc. **127**, 14454–14465 (2005)

18. Pramanik, M., Li, C., Imura, M., Malgras, V., Kang, Y.-M., Yamauchi, Y.: Ordered mesoporous cobalt phosphate with crystallized walls toward highly active water oxidation electrocatalysts. Small **12**, 1709–1715 (2016)
19. Yu, J.C., Zhang, L., Zheng, Z., Zhao, J.: Synthesis and characterization of phosphated mesoporous titanium dioxide with high photocatalytic activity. Chem. Mater. **15**, 2280–2286 (2003)
20. Tian, B., Liu, X., Tu, B., Yu, C., Fan, J., Wang, L., Xie, S., Stucky, G.D., Zhao, D.: Self-adjusted synthesis of ordered stable mesoporous minerals by acid-base pairs. Nat. Mater. **2**, 159–163 (2003)
21. Liu, G., Jia, M.J., Zhou, Z., Wang, L., Zhang, W.X., Jiang, D.Z.: Synthesis and pore formation study of amorphous mesoporous aluminophosphates in the presence of citric acid. J. Colloid Interface Sci. **302**, 278–286 (2006)
22. Wilke, M., Batzdorf, L., Fischer, F., Rademann, K., Emmerling, F.: Cadmium phenylphosphonates: preparation, characterisation and in situ investigation. RSC Adv. **6**, 36011–36019 (2016)
23. Wilke, M., Buzanich, A.G., Reinholz, U., Rademann, K., Emmerling, F.: The structure and In Situ synthesis investigation of isomorphic mononuclear molecular metal phenylphosphonates. Dalton Trans. **45**, 9460–9467 (2016)
24. Huang, X., Wu, S.S., Ke, X.K., Li, X.Y., Du, X.Z.: Phosphonated pillar[5]arene-valved mesoporous silica drug delivery systems. ACS Appl. Mater. Interfaces **9**, 19638–19645 (2017)
25. Rim, H.P., Min, K.H., Lee, H.J., Jeong, S.Y., Lee, S.C.: pH tunable calcium phosphate covered mesoporous silica nano containers for intracellular controlled release of guest drugs. Angew. Chem. Int. Ed. **50**, 8853–8857 (2011)
26. Zhang, M.J., Zhang, L.Y., Chen, Y.D., Li, L., Su, Z.M., Wang, C.G.: Precise synthesis of unique polydopamine/mesoporous calcium phosphate hollow janus nanoparticles for imaging-guided chemo-photothermal synergistic therapy. Chem. Sci. **8**, 8067–8077 (2017)
27. Colodrero, R.M.P., Olivera-Pastor, P., Cabeza, A., Bazaga-Garcia, M.: Properties and applications of metal phosphates and pyrophosphates as proton conductors. Materials **15**, 1292 (2022)
28. Bhanja, P., Na, J., Jin, T., Lin, J., Wakihara, T., Bhaumik, A., Yamauchi, Y.: Chem. Mater. **31**(15), 5343–5362 (2019)
29. Colomban, P.: Chemistry of solid-state materials. In: Proton Conductors: Solid, Membranes and Gels-Materials and Devices, p. 581. Cambridge University Press, Cambridge, UK (1992)
30. Fragua, D.M., Castillo, J., Castillo, R., Vargas, R.A.: New amorphous phase $KnH_2PnO_{3n+1}(n\gg 1)$ in KH_2PO_4. Rev. Latin Am. Metal. Mat. **2**, 491–497 (2009)
31. Li, J., Yi, M., Zhang, L., You, Z., Liu, X., Li, B.: Energy related ion transports in coordination polymers. Nano Select. 1–19 (2021)
32. Sazali, N., Salleh, W.N.W., Jamaludin, A.S., Razali, M.N.M.: New perspectives on fuel cell technology: a brief review. Membranes **10**, 99 (2020)
33. Dupuis, A.-C.: Proton exchange membranes for fuel cells operated at medium temperatures: materials and experimental techniques. Prog. Mater. Sci. **56**, 289–327 (2011)
34. Han, X., Xie, Y., Liu, D., Chen, Z., Zhang, H., Pang, J., Jiang, Z.: Synthesis and properties of novel poly(arylene ether)s with densely sulfonated units based on carbazole derivative. J. Membr. Sci. **589**, 117230 (2019)
35. Loreti, G., Facci, A.L., Ubertini, S.: High-efficiency combined heat and power through a high-temperature polymer electrolyte membrane fuel cell and gas turbine hybrid system. Sustainability **13**, 12515 (2021)
36. Peighambardoust, S.J., Rowshanzamir, S., Amjadi, M.: Review of the proton exchange membranes for fuel cell applications. Int. J. Hydrog. Energy **35**, 9349–9384 (2010)
37. Aslan, A., Bozkurt, A.: Nanocomposite membranes based on sulfonated polysulfone and sulfated nano-titania/NMPA for proton exchange membrane fuel cells. Solid State Ion. **255**, 89–95 (2014)
38. Jin, Y.G., Qiao, S.Z., Xu, Z.P., da Costa, J.C.D., Lu, G.Q.: Porous silica nanospheres functionalized with phosphonic acid as intermediate-temperature proton conductors. J. Phys. Chem. C **113**, 3157–3163 (2009)

39. Bao, S.S., Li, N.Z., Taylor, J.M., Shen, Y., Kitagawa, H., Zheng, L.M.: Co-Ca phosphonate showing humidity-sensitive single crystal to single crystal structural transformation and tunable proton conduction properties. Chem. Mater. **27**, 8116–8125 (2015)
40. Wei, Y.S., Hu, X.P., Han, Z., Dong, X.Y., Zang, S.Q., Mak, T.C.W.: Unique proton dynamics in an efficient MOF-based proton conductor. J. Am. Chem. Soc. **139**, 3505–3512 (2017)
41. Alberti, G., Casciola, M., Pica, M., Tarpanelli, T., Sganappa, M.: New preparation methods for composite membranes for medium temperature fuel cells based on precursor solutions of insoluble inorganic compounds. Fuel Cells **5**, 366–374 (2005)
42. Pili, S., Argent, S.P., Morris, C.G., Rought, P., Garcia-Sakai, V., Silverwood, I.P., Easun, T.L., Li, M., Warren, M.R., Murray, C.A., Tang, C.C., Yang, S.H., Schroder, M.: Proton conduction in a phosphonate-based metal-organic framework mediated by intrinsic "free diffusion inside a sphere." J. Am. Chem. Soc. **138**, 6352–6355 (2016)
43. Begum, S., Wang, Z.Y., Donnadio, A., Costantino, F., Casciola, M., Valiullin, R., Chmelik, C., Bertmer, M., Kaerger, J., Haase, J., Krautscheid, H.: Water-mediated proton conduction in a robust triazolyl phosphonate metal-organic framework with hydrophilic nanochannels. Chem. Eur. J. **20**, 8862–8866 (2014)
44. Zhou, T., Du, Y., Yin, S., Tian, X., Yang, H., Wang, X., Liu, B., Zheng, H., Qiao, S., Xu, R.: Nitrogen-doped cobalt phosphate@ nanocarbon hybrids for efficient electrocatalytic oxygen reduction. Energy Environ. Sci. **9**, 2563–2570 (2016)
45. Zhou, T.H., Du, Y.H., Wang, D.P., Yin, S.M., Tu, W.G., Chen, Z., Borgna, A., Xu, R.: Phosphonate-based metal-organic framework derived Co-P-C hybrid as an efficient electrocatalyst for oxygen evolution reaction. ACS Catal. **7**, 6000–6007 (2017)
46. Zhang, R., El-Refaei, S.M., Russo, P.A., Pinna, N.: Metal phosphonate coordination networks and frameworks as precursors of electrocatalysts for the hydrogen and oxygen evolution reactions. J. Nanopart. Res. **20**, 146 (2018)
47. Cai, Z.X., Xu, W., Li, F.M., Yao, Q.H., Chen, X.: Electropolymerization fabrication of Co phosphate nanoparticles encapsulated in N, P-codoped mesoporous carbon networks as a 3D integrated electrode for full water splitting. ACS Sustain. Chem. Eng. **5**, 571–579 (2017)
48. Pan, D.-S., Chen, P., Zhou, L.-L., Liu, J.-H., Guo, Z.-H., Song, J.-L.: Self-template construction of 2D amorphous N-doped CoFe-mesoporous phosphate microsheets for zinc-air batteries. J. Power Sources **498**, 229859 (2021)
49. Mayr, H.O., Klehm, J., Schwan, S., Hube, R., Suedkamp, N.P., Niemeyer, P., Salzmann, G., von Eisenhardt-Rothe, R., Heilmann, A., Bohner, M., Bernstein, A.: Microporous calcium phosphate ceramics as tissue engineering scaffolds for the repair of osteochondral defects: biomechanical results. Acta Biomater. **9**, 4845–4855 (2013)
50. Rezwan, K., Chen, Q.Z., Blaker, J.J., Boccaccini, A.R.: Biodegradable and bioactive porous polymer/inorganic composite scaffolds for bone tissue engineering. Biomaterials **27**, 3413–3431 (2006)

Hierarchically Porous Metal Phosphates and Phosphonates: Emerging Materials Toward Advance Applications

Umair Azhar, Muhammad S. Bashir, Muhammad Arif, and Muhammad Sagir

Abstract The ability to create hierarchically porous nanostructures using materials based on metal phosphate and phosphonates is very astonishing. The major drivers of the scientific community are focused on the need to rationalize novel synthetic ways to synthesize these materials under controlled settings especially related to morphology. In this chapter, we have highlighted different synthetic techniques that have been employed in the synthesis of metal phosphonates and how the properties of porous metal phosphonates and phosphates are being impacted. Nanoporous metal phosphonates are proliferating rapidly owing to their versatile applications in different areas, including energy storage, catalysis, environmental intervention, and biology, among others, which are also discussed in this chaptesr. It is expected that the chemistry of porous metal phosphonates and phosphates would advance as a result of their utilization in domains like biology and fuel cells.

Keywords Hierarchical · Porous nanostructures · Phosphates · Phosphonates · Fuel cells

1 Introduction

The research in the field of inorganic–organic hybrid materials has expanded over the last two decades, thanks to the advent of hierarchically porous materials including metal–organic frameworks (MOFs) [1–3]. Hybrid materials have a lot of potential

---

U. Azhar · M. Arif · M. Sagir
Institute of Chemical and Environmental Engineering, Khwaja Fareed University of Engineering and Information Technology, Rahim Yar Khan 64200, Punjab, Pakistan

M. S. Bashir (✉)
Institutes of Physical Science and Information Technology, Key Laboratory of Structure and Functional Regulation of Hybrid Materials of Ministry of Education, Anhui University, Hefei 230601, Anhui, China
e-mail: engr_sohailbashir@yahoo.com; sohail14@ustc.edu.cn

CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, Anhui, China

R. K. Gupta (ed.), *Metal Phosphates and Phosphonates*, Engineering Materials,
https://doi.org/10.1007/978-3-031-27062-8_2

in both material chemistry and daily applications. Fine-tuning the matrix and interfacial characteristics of both organic and inorganic processes have been made easy. Modification of chemical or physical properties or the ability to manipulate specific chemical reactions or interactions is possible. As a result, hybrid porous materials like MOFs have been employed in many research reports. The class of chemicals synthesized via the reaction of metals and organophosphonic units is called porous metal phosphonates and is noteworthy since it is more specific and has been less researched. With their malleable surfaces, tunable pore sizes, readily accessible channels, and controllable pore environments, porous materials are used in a wide range of proven applications and cutting-edge technologies to address complex economic and energy challenges [4–9].

Structures of hybrid porous metal phosphonates are shown in Fig. 1, and these structures are compared in great detail to those of many other common materials. The unique inorganic–organic hybrid structure of porous metal phosphonates makes them stand out from others of the same rank [11, 12]. There are various types of porous materials, but porous metal phosphonates stand out by their unique properties [13]. Beyond the straightforward physical pairings of organic in organic–inorganic metal with holes, especially phosphonates, the molecular interweaving of organic and inorganic components in nanocomposites goes a step further. This is because nanocomposites include both organic and inorganic materials in their molecular interweaving. To sum up, hybrid porous metal phosphonates have the best features of both organic and inorganic frameworks. All other properties of MOFs are equivalent to those of porous organic–inorganic metal phosphonates by taking advantage of the malleability of organic chemistry to get the superior chemical and physical stability it provides [14–16]. The benefits of porous metal phosphonates over other forms of porous materials are their chemical versatility and their low processing complexity. In addition, the development of metal phosphonates over the last two decades, beginning with layered metal phosphonates and progressing via phosphonates-based metal–organic frameworks and onto templated (supramolecular) mesoporous metal phosphonates is of worthy discussion. From layered metal phosphonates to phosphonate-containing metal–organic frameworks, this transformation is rather extensive. The degree of long-range organization and the presence or absence of pores in a polymeric network is two additional criteria that may be used to classify such a network. Metal-layered phosphonates, metal–organic frameworks with phosphonates, and templated (supramolecular) metallic phosphonates are all included in this evolution.

2 Synthesis of Porous Metal Phosphonates

Prior to the metal phosphonates, we will discuss some of the metal phosphonate networks produced in recent years and the challenges faced in obtaining these networks. In this section, we address the three distinct structural morphology classes

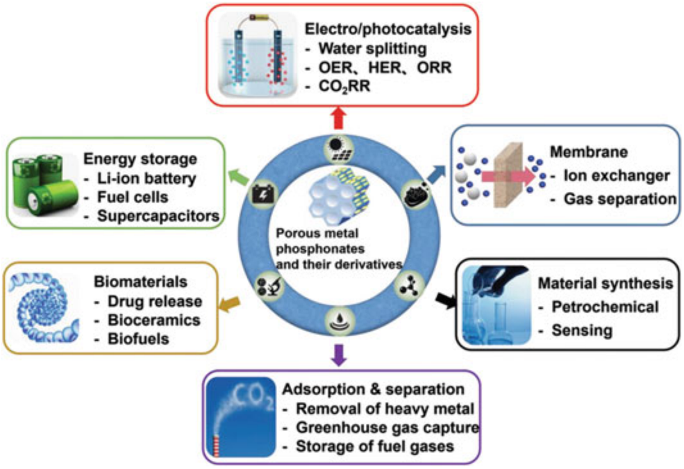

Fig. 1 Characteristics of porous metal phosphonates also comparison to other common materials. Adapted with permission [10]. Copyright (2021), Wiley–VCH

(Fig. 2) that are dictated by the conditions under which the porous metal phosphonates are synthesized, as well as the precursors and kind of organophosphonic acid utilized.

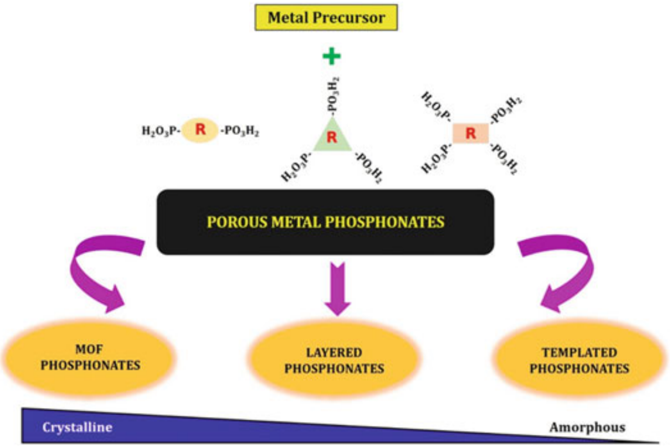

Fig. 2 Classification of porous metal phosphonate based on structural morphological properties. Adapted with permission [17]. Copyright (2021), MDPI

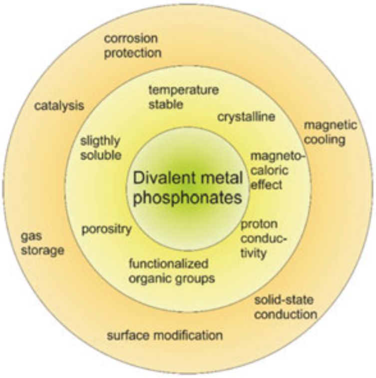

Fig. 3 Divalent metal phosphonates: Recent advances in synthesis, on-site characterization, and structural determination**.** Adapted with permission [19], Copyright (2016), De Gruyter

2.1 Layered Metal Phosphonates

Similar to the process used to produce metal phosphates, layered metal phosphonates were created by directly precipitating metal precursors and organophosphonic acids [18]. Similar to layered metal phosphates, but without the interlayer of stacked metal phosphates, the morphologies of resulting compounds were studied. The preparation of divalent and trivalent metal phosphonates will be covered first, followed by tetravalent phosphonates. One key difference is how metal ions react in certain solvents. It is to be noted that there is a robust interplay between phosphoric acid and transition metals. However, when tetravalent metal precursors speed up the formation of a metal phosphonate coordination network, uncontrolled precipitation of the combinations occurs, even under highly acidic circumstances, destroying the regulated structural features. To crystallize, however, phosphonic precursors must first have their metal moieties sufficiently solubilized to allow for uniform interactions with the other molecules during the controlled assembly of these molecules into a hybrid network. When this happens, only the phosphonic precursors will be able to solidify. Multiple methods for the modern synthesis, characterization, and solution of divalent metal structures are shown in Fig. 3. A decrease in the pH of the reaction fluid may be employed to reduce the concentration of divalent and trivalent metals during synthesis.

2.2 MOFs–Phosphonates

In structures consisting of metal nodes and organo-functional units, metal–organic frameworks are a prominent type of coordination polymeric networks known for their high surface areas and permeability. Specific classes of MOFs, those with metallic units joined by phosphonates are promising materials. When compared to carboxylate MOFs, which have been available since the late 1990s, metal phosphonate-based