# Synthesis and Electrochemical properties of metal(II)-
carboxyethylphenylphosphinates

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Synthesis and Electrochemical properties of metal(II)-
carboxyethylphenylphosphinophosphinates

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We report herein the synthesis, structural characterization and electrocatalytic properties of three new coordination polymers, resulting from the combination of divalent metal [Ca2+, Cd2+ or Co2+] salts with (2-carboxyethyl)(phenyl)phosphinic acid. In addition to the usual hydrothermal procedure, the Co2+ derivative could be also prepared by microwave-assisted synthesis, in much shorter times. The crystal structures were solved ab initio, from powder diffraction data. Compounds M2[O2P(CH2CH2COOH)(C6H5)]2 (M = Cd (1) or Ca (2)) crystallize in the monoclinic system and display a layered topology, with the phenyl groups pointing toward the interlayer space in a interdigitated fashion. Compound Co2[O2P(CH2CH2COO)(C6H5)(H2O)]·2H2O (3) presents a 1D structure composed of zig-zag chains, formed by edge-sharing cobalt octahedra, with phenyl groups pointing outside. Packing of these chains is favored by hydrogen bond interactions via lattice water. In addition, H-bonds along the chains are established with participation of the water molecules and the hydrophilic groups from the ligand. However, the solid exhibits a low proton conductivity, attributed to the isolation of the hydrophilic regions caused by the arrangement of hydrophobic phenyl groups. Preliminary studies on the electrocatalytical performance for the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) have been conducted for compound 3 and its pyrolytic derivatives, which were previously throughout characterized. By comparison, another Co2+-phosphinate, 4, obtained by microwave-assisted synthesis, but with distinct stoichiometry and known structure was also tested. For OER, the best performance was reached with a derivative of 3, prepared by heating this compound in N2 at 200 °C. This derivative presented overpotential (339 mV, for a current density of 10 mA·cm⁻²) and Tafel slope (51.7 mV·dec⁻¹) values comparable to other Co2+ related materials.

Introduction

To date, only few papers dealing with synthesis and properties of metal phosphinates have been published,1 in contrast to the analogous multifunctional phosphonates-based coordination polymers, which have been profusely studied for several applications, among them proton conductors for Fuel Cells, electrodes for batteries and catalysts.2 Available data on metal phosphinates indicate that the dimensionality of these solids is highly dependent on the type of the phosphinic acid (R2R2POOH) employed. So, monophosphinic acids usually lead to 1D solids, transition metal bisphosphinates form 2D networks,3,4 whereas multifunctional ligands like those having both, carboxylic and phosphinic groups, e.g., (2-carboxyethyl)(phenyl)phosphinic acid, give rise to 2D or 3D networks.5-9 By employing the latter ligand, Mn2+- and Co2+- derivatives, M3(L)(OH)2, with interesting magnetic properties were obtained.5 Moreover, uranyl carboxyphosphinate derivatives, containing auxiliary N-donor ligands, showed promising physicochemical properties, including photoluminescence, photocatalytic properties, as well as relevant characteristics relative to the waste management and separation procedures of nuclear fuel.10 Using the linker phenylene-1,4-bis(methylphosphinic acid), porous metal phosphinates have been recently reported and, more important, this porosity was shown to be dependent on the size of the organic groups.11 Finally, by using auxiliary ligands,12-14 a porous tubular 1D was synthesized from the reaction of a Cu(II) salt with the ligand 1,2-bis(4-pyridyl)ethane and P,P'-diphenyl-diphosphinate.15

On the other hand, phosphorus-containing coordination polymers have attracted attention as precursors, for obtaining versatile carbon-based materials, which are usable as electrocatalysts for fuel cells, electrolyzers or metal–air...
batteries. These materials have been tested in key processes, such as the oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and hydrogen evolution reaction (HER).\textsuperscript{16-18} Furthermore, the electrocatalytic activity was found to be enhanced by heteroatom-doping of the carbon residues.\textsuperscript{19,20} In line with this, ligands 1-Hydroxyethylidene-1,1-diphosphonic acid and pyrazine have been jointly employed to synthesize a copper derivative that, upon pyrolysis in N\textsubscript{2}, transformed in Cu nanoparticles supported on N,P co-doped porous carbon.\textsuperscript{21} In this paper, we report the hydrothermal and/or microwave-assisted synthesis and their the structural characterization for three new carboxyethylphosphynophosphinates of Ca, Cd and Co(II). In addition, we report, for the first time, preliminary results on the electrocatalytic behavior of two Co (II) phosphinate derivatives, one of them already structurally described in literature, for OER and ORR.

**Experimental**

**Materials**

Dichlorophenylphosphine, acrylic acid, cobalt acetate tetrahydrate, calcium acetate monohydrate, copper acetate monohydrate, cadmium acetate dihydrate and magnesium chloride were purchased from Sigma-Aldrich. All reagents were used without further purification.

**Synthesis**

Preparation of 2-Carboxyethylphosphinic acid (CEPPA). The acid was prepared from dichlorophenylphosphine and acrylic acid, according to literature.\textsuperscript{22}

Preparation of Cd[O\textsubscript{2}P(CH\textsubscript{2}CH\textsubscript{2}COO)](C\textsubscript{6}H\textsubscript{5}H\textsubscript{12})\textsubscript{2} (1). A mixture of 2.2 mmol Cd(CH\textsubscript{3}COO\textsubscript{2})\textsubscript{2}, 2H\textsubscript{2}O, 1.0 mmol MgCl\textsubscript{2}, 4 mmol (2-Carboxyethylphosphinic acid), 8 mmol NaF, 70 mmol CH\textsubscript{3}COOH and 16 ml of distilled water (DI) was heated at 120 °C for 36 h in a Teflon autoclave. After cooling at room temperature, the solid was isolated by filtration, washed several times with DI and dried at room temperature. Elemental composition (wt%): Anal. calcd for CaC\textsubscript{53}H\textsubscript{80}O\textsubscript{10}P\textsubscript{2}: C 60.74; found C 60.65.

Preparation of Ca[O\textsubscript{2}P(CH\textsubscript{2}CH\textsubscript{2}COO)(C\textsubscript{6}H\textsubscript{5}H\textsubscript{12})\textsubscript{2}]COO (2) and [Co\textsubscript{2}(O\textsubscript{2}P(CH\textsubscript{2}CH\textsubscript{2}COO)(C\textsubscript{6}H\textsubscript{5}H\textsubscript{12})\textsubscript{2}]H\textsubscript{2}O]\textsubscript{2}H\textsubscript{2}O (3). 3 mmol Ca(CH\textsubscript{3}COO\textsubscript{2})\textsubscript{2}, H\textsubscript{2}O or Co(CH\textsubscript{3}COO\textsubscript{2})\textsubscript{4}H\textsubscript{2}O were dissolved in 10 ml distilled water and 3 mmol (2-carboxyethylphosphinic acid) were dissolved also in 10 ml distilled water under moderate heating (60 °C). The solutions were mixed and kept under stirring for 1 hour at 50-60 °C then transferred in a stainless steel autoclave with a teflon autoclave (ca. 30 ml capacity) and kept at 130 °C for 24 hours. The obtained solids were filtered, washed with DI several times and air-dried at room temperature. Elemental composition (wt%): Anal. calcd for CaC\textsubscript{53}H\textsubscript{80}O\textsubscript{10}P\textsubscript{2}: C 46.36, H 4.32; found C 45.96, H 4.21.

Alternatively, compound 3 was also prepared by microwave assisted synthesis (Anton Paar Monowave 300 microwave) by reaction of the mixture in a 30 ml glass vial at 150 °C for 5 minutes and under constant magnetic stirring (600 rpm). The solid was recovered by centrifugation, washed with DI water and dried at room temperature. Longer reaction times (1h) led to the reported compound, Co\textsubscript{2}[O\textsubscript{2}P(CH\textsubscript{2}CH\textsubscript{2}COO)(C\textsubscript{6}H\textsubscript{5}H\textsubscript{12})\textsubscript{2}]COO (4).

**Chemical and Physical Characterization.** Elemental analyses (C, N and H) were performed with a Perkin-Elmer 240 analyzer. TG-DTA analysis were recorded on an SDT-Q600 (TA instruments). The temperature varied from RT to 1000 °C with a heating rate of 10 °C·min\textsuperscript{-1}. Measurements were carried out on samples in open platinum crucibles under a flow of air or N\textsubscript{2}. Infrared spectra were recorded in the 4000 - 500 cm\textsuperscript{-1} range at 2 cm\textsuperscript{-1} resolution (64 scans accumulated) using an ATR accessory (Golden Gate Single Reflection Diamond ATR System) coupled to FTIR spectrometer (Vertexde Bruker).

**X-ray diffraction characterization.** The crystal structure of these compounds were determined from synchrotron X-ray powder diffraction data (SRXRD) or laboratory X-ray powder diffraction data (LXRPD). For 3, SRXRD were collected at the high resolution BL04-MSPD beamline of ALBA, the Spanish Synchrotron Radiation Facility (Barcelona, Spain). A wavelength of 0.4124 Å was selected with a double-crystal Si (111) monochromator and determined from a Si640d NIST standard (a = 5.43123 Å) measurements, using a MYTHEM detector. The capillary was rotated during data collection to improve diffraction particle statistics and patterns were collected over the angular range 1.70 – 20° (2θ) or the d-space of 1.19-13.82Å. For the other compounds, 1 and 2, LXRPD were collected on a D8 ADVANCE (Bruker AXS) diffractometer equipped with a Johansson Ge(111) primary monochromator giving a monochromatic Mo radiation (λ = 0.7093 Å) and using the energy-dispersive linear detector LYNXEYE XE 500 μm. Data were collected in the angular region 4.40 – 50° (2θ) or the d-space of 0.84-9.21Å, with a step size of 0.01° and a counting time of ~1600 s/step.

For samples 2 and 3, their crystal structures were solved by direct methods using the program EXPO2014.\textsuperscript{23} The starting framework models, containing all atoms in the asymmetric part of the unit cell except those corresponding to water in case of 3, were derived from interpretation of the electron density map computed with the set of refined phases with the highest combined figure of merit. For cadmium derivative, 1, its crystal structure was obtained by simulated annealing procedure implement in EXPO2014\textsuperscript{23} and using the structure of the orthorhombic polymorph\textsuperscript{24} as starting model. The initial structural models were refined by the Rietveld method,\textsuperscript{25} using the GSAS package\textsuperscript{26} and the EXPGUI graphic interface.\textsuperscript{27} The following soft constraints were imposed in order to preserve chemically reasonable geometries for the phosphinate, alkyl chain, and aromatic ring: /PO\textsubscript{2}C\textsubscript{2} tetrahedron/P-O /S.15(1) Å, P-C /S.80(1) Å, O-O /S.55(1) Å, O-C /S.73(2) Å, C1-C2//S.90(2) Å; /C1-C2-C300 group/C-C /S.50(1) Å, C1-C3 /S.50(2) Å, C3- Ocarb /S.21(3) Å, Ocarb-Ocarb /S.21(2) Å and C2-Ocarb /S.26(2) Å and /aromatic ring/ C-C /S.40(1) Å, C Ring-C Ring /S.40(1) Å, C Ring-C Ring /S.80(1) Å. No attempts to locate the H atoms were carried out due to the limited quality of the XRPD data. For 1 and 3, the final weight factor for the soft constraints was 10 and...
three isotropic atomic displacement parameters were refined, one for the metal atom, a second for the P atoms and a third one for the rest of the atoms. For 2, the final weight factor for the soft constrains was 15 and only two isotropic atomic displacement parameters were refined, one for the heavier atoms (Ca and P) and a second one for the rest of the atoms. Selected structural data are reported in Table 1 and the final Rietveld plot is given in the Supporting Information (SI) as Figures S1-S3. Thermodiffactometric data were obtained in an Anton Paar HTK1200N Camera, under static air, on a PANanalytical X’Pert Pro automated diffractometer. Data were collected in Bragg-Brentano reflection configuration, with Cu Kα₁ and the X’Celerator detector. Data were collected at different temperature intervals from room temperature up to 180 °C for 3. A heating rate of 5 °C·min⁻¹ and a delay time of 5 minutes to ensure thermal stabilization were used. PXRD patterns were recorded in the region 4 - 70° (2θ), with a step size of 0.017° - 0.033° and an equivalent counting time of ~57 – 100 s/step.

Table 1 Crystallographic Data and Structure Refinements for M-CEPPA derivatives

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<th>Chemical formula</th>
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<th>β (°)</th>
<th>γ (°)</th>
<th>V (Å³)</th>
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**XPS characterization.** The surface composition and chemical environment were carried out by X-ray photoelectron spectroscopy. Analyses were performed on a Physical Electronics ESCA 5701 spectrometer.

**Proton Conductivity Studies.** Impedance measurements of the powdered polycrystalline compounds were carried out on cylindrical pellets (~5 mm diameter; ~1.22–0.73 mm thickness) obtained by pressing ~30–40 mg of sample at 250 MPa for 1 min between porous C electrodes (Sigracet, GDL 10 BB, no Pt). Pellets were placed inside a temperature and humidity controlled chamber (Espec SH-222). Impedance data were collected using an AUTOLAB PGSTAT302N impedance analyzer equipped with a Frequency Response Analyzer (FRA) module over the frequency range from 20 Hz to 1 MHz with an applied voltage of 0.35V. All measurements were electronically controlled by the Nova package of programs. In order to equilibrate the water content, pellets were first preheated (0.2 °C/min) from 25 to 80 °C at 95 %RH. Impedance spectra were recorded on cooling using stabilization times of 5 h for each temperature (80, 70, 60, 50, 40, 30 and 25 °C). Water condensation on the sample was avoided by reducing first the relative humidity before decreasing temperature. The total pellet resistance (Rₚ) was obtained by fitting to the equivalent circuit models from the Nyquist plots at different temperatures.

**Electrochemical measurements.** Electrochemical measurements for compounds 3 and 4 were carried out with a BioLogic VSP-128 potentiostat/galvanostat having a built-in electrochemical impedance spectroscopy analyzer. The electrochemical activity of the catalysts was measured in a typical three-electrode configuration using a 5 mm diameter glassy carbon rotating disc electrode (RDE, area= 0.196 cm², Methrom Autolab) as working electrode and the platinum rod and Ag/AgCl (3M KCl) electrode used as the counter and reference electrodes, respectively. For the preparation of the working electrode, 4 mg of catalysts and 1.3 mg of carbon black (Super P® Conductive, <99%, Alfa Aesar) were dispersed into 470 μL of ethanol/H₂O (v/v = 1/1, Milli-Q Water, 18 MΩ·cm⁻¹ and ethanol, >99.5%, Sigma Aldrich) with 30 μL of 5 wt% Nafion® solution (Nafion® 117 solution, Sigma Aldrich) followed by sonication for 30 min to obtain a homogeneous ink. Then, 8.2 μL of the catalyst ink was spread out on the glassy carbon electrode by drop-coating and dried at room temperature to achieve a catalyst loading of 0.33 mg·cm⁻². For comparison, commercial 20 wt% Pt/C (HISPEC 3000, Johnson Matthey Company) was deposited on the glassy carbon with the same loading. Prior to catalyst deposition, the GC electrode was polished with 0.3 μm alumina slurry and then rinsed with deionized water and ethanol, sonicated for 3 min, and dried in air. All the current densities were normalized to the geometrical surface area of the electrodes, and the measured potential (versus Ag/AgCl) was converted to the potential (versus reversible hydrogen electrode, RHE) according to the Nernst equation [E(RHE) = E(Ag/AgCl) + 0.205 + 0.059pH]. All the electrochemical measurements were conducted with iR compensation. The OER tests were performed in 1M KOH (KOH pure pellets, Sigma Aldrich) electrolyte at 25 °C with the RDE rotate at 1600
rpm. Cyclic voltammograms (CVs) and linear sweep voltammograms (LSVs) were measured at a scan rate of 20 and 10 mV s\(^{-1}\) respectively in the potential window 1.0 to 1.7 V vs RHE. The overpotential was determined from the equation of \(\eta = E_{(RHE)} - 1.23\). The Tafel slope was calculated according to the Tafel equation: \(\eta = a + b \log J\) where \(a\), \(b\), and \(J\) correspond to the overpotential, Tafel slope and the current density, respectively. Electrochemical impedance spectroscopy (EIS) measurements were carried out from 100 kHz to 0.1 Hz with an amplitude of 5 mV at 1.58 V vs RHE. Likewise, the ORR tests were conducted in 0.1M KOH electrolyte at 25 °C with the RDE rotate at 1600 rpm. Cyclic voltammograms (CVs) and linear sweep voltammograms (LSVs) were measured at a scan rate of 20 and 10 mV s\(^{-1}\) respectively in the potential window 0.2 to 1.2 V vs RHE. The catalyst supported on carbon paper (1x1 cm\(^2\)) with 1 mg cm\(^{-2}\) loading was used to perform stability tests. Prior to the OER and ORR tests, the KOH electrolyte was bubbled for 30 min with \(\text{N}_2\) and \(\text{O}_2\) respectively and maintained over the whole measurement to ensure the gas saturation in the electrolyte. The turnover frequency number (TOF) was obtained from the expression: \(\text{TOF} = i/4Q\), where \(i\) is the current intensity and \(Q\) is the faradaic charge under the baseline-corrected voltammetric peak preceding the electrocatalytic wave, and assuming a faradaic efficiency of 100%.\(^{24}\)

Results and discussion

Although the general method of synthesis for these compounds is a hydrothermal reaction for 24 h, crystalline Co(II) derivatives were also prepared by fast microwave-assisted synthesis within 60 min. The cadmium derivative here reported is a new polymorph of another one described elsewhere.\(^{24}\) This polymorph, that crystallizes in the orthorhombic system (space group Pca2\(_1\)), was obtained by hydrothermal reaction at 120 °C, instead of 150 °C, and in the presence of a (0.0625 M) MgCl\(_2\) solution, used to test the possibility of formation of solid solution derivatives. Although present in the solid, as revealed by SEM-EDX analysis, the Mg\(^{2+}\) ion does not incorporate to the crystal structure, but it is part of an accompanying amorphous impurity, which is responsible for a decrease in carbon percentage, relative to the pure crystalline solid.

On the other hand, the IR spectra of compounds 1 and 2 (Figure S4) show a band at 1683 cm\(^{-1}\), which is absent in spectra of 3 and 4, indicative of the presence of a carboxylic group. For solid 3, broad bands in the region of 3495 - 3322 cm\(^{-1}\), together with the deformation vibration of H-O-H at 1638 cm\(^{-1}\), indicate the presence of H-bonded water, in agreement with crystallographic data (see below). Other bands characteristic of phosphinate groups are also observed in the IR spectra.\(^{24}\)

Crystal structure of M\(^{111}\)(O\(_3\)P(CH\(_2\)\(_2\)COOH)(C\(_6\)H\(_5\))\(_2\))\(_3\), M\(^{111}\)= Cd (1) and Ca (2).

Compounds 1 and 2 crystallizes in the monoclinic system, with similar \(a\) and \(b\) unit cell parameters, which define the organic-inorganic layers. Packing of the layers takes place along \(c\) axis direction, but in 1, the \(c\) parameter is twofold (Table 1). Their crystal structures, solved \textit{ab initio} from laboratory powder diffraction data, contain 29 non-hydrogen atoms in the asymmetric part of the unit cell, one M\(^{2+}\) ion and two (Ph-PO\(_2\)-C\(_6\)H\(_4\)-COOH\(^-\))\(^+\) ligands crystallographically independent (Figure 1). Both compounds exhibit similar structural characteristics with divalent cation in a distorted octahedral environment (Table S1) surrounded by four phosphinate oxygen atoms and two carboxylate oxygen atoms from six ligands. The layers are composed of chains of isolated MO\(_6\) polyhedra interconnected by bridging phosphinate groups, into a near-planar 8-membered ring (A), along the \(b\) direction (Figure 1) with intra-chain M\(^{111}\)–M\(^{3+}\) distances (d\(_J\)) of 5.52 Å (Cd\(^{3+}\)) and 5.77 Å (Ca\(^{2+}\)). Neighbouring chains are interconnected by monodentate alkyl carboxylic groups, along the \(a\)-axis direction, forming 14-membered rings (B) between two metal centres and two ligands. In the \(a\) direction, the M\(^{3+}\)–M\(^{3+}\) distance is kept at \(\sim 7.60\) Å (d\(_J\)), while in the cadmium derivative two different slightly distances are found, at 7.57 and 7.60 Å. This M\(^{2+}\)-ligand connectivity mode has been also reported for other cadmium phosphinates, including the orthorhombic polymorph.\(^{24}\)

![Figure 1](image.png)
The phenyl rings point toward the interlayer space and they arrange, between adjacent layers, in an interdigitated fashion and rotated slightly to each other, with short C–C distances, of 3.30 Å for 1 and 3.15 Å for 2 (Figure 1 and S5).

**Structure of Co₂[(O₆P(Ph₂CH₂COO))(C₆H₅)[H₂O]]·2H₂O (3)**

This compound crystallizes in the $P2_1/a$ (N° 14) space group (see Table 1), and contains 35 non-hydrogen atoms in the asymmetric unit: three crystallographically independent Co²⁺ ions, two of them (Co1 and Co2) in special position, two (Ph-PO₂-C₆H₅-COO⁻) ligands, and four water molecules (Figure 2). In contrast with the layered derivative previously reported,⁵ that we have obtained by an alternative microwave assisted method (compound 4), solid 3 displays a monodimensional structure consisting of CoO₆ polyhedra chains, with the phenyl groups pointing outside, as shown in Figure 2. The zig-zag chains are built up of edge-sharing Co²⁺ octahedra extended along the c axis direction. More precisely, these chains can be described as Co3-Co2-Co3 trimeric units linked through Co1. The coordination environment of Co1 and Co2 atoms are made-up exclusively by oxygens from the phosphinate ligand, whereas for Co3 atom, four oxygen atoms from four different ligands and two water oxygens (Ow1 and Ow2) form the octahedral environment. Each (Ph-PO₂-C₆H₅-COO⁻) anion acts as a bidentate ligand for Co1, through an oxygen atom from the phosphinate group (O11) and an oxygen atom (O41), most probably the non-protonated one, from the carboxylic group. In addition, O11 and O41 bridge Co1 and Co3 given rise to a shared edge between both cobalt atoms (Figure 2). Furthermore, the oxygen O21 from the phosphinate group binds monodentately to Co2. This metal-ligand connectivity is quite similar to that of Co(II) phenyl(carboxymethyl)phosphinate monohydrate, [Co₂(PhPO₂-C₆H₅-CO₂)₂(H₂O)]·H₂O,⁶ indicating that the connectivity can be preserved by hosting more lattice water molecules upon increasing the length of ligand alkyl chain.

The phosphonate groups are situated alternatively up and down of the Co atoms plane, with the phenyl groups in between the chains being rotated to each other, preventing thus establishing π–π interactions between aromatic rings of the same chain (Figure 2).

Each chain is surrounded by other six ones, with weak Van de Waals interactions between the phenyl groups. This arrangement forms isolated hydrophilic regions separated by hydrophobic environments of phenyl groups. H-bond interactions take place along a single chain between lattice water, coordinated water and unbound oxygen atom from the carboxylate group. In addition, interchain H-bonds are established through the lattice water (Table S2, Figure 2).

![Figure 2](image)

**Figure 2.** (a) Coordination environments for Co²⁺ atoms and metal-ligand connectivity for 3; (b) 1D arrangement of the chains running along the c-axis; (c) packing of the 1-D chains; (d) H-bond network in the hydrophilic region: O₂/C tetrahedra, orange; CoO₆ octahedra, green.

**Electrochemical characterization**

The cobalt phosphinates (compounds 3 and 4) were selected to evaluate their electrochemical properties, as cobalt electrocatalysts have been shown promising in OER and ORR processes.⁰³⁻³² We first carried out proton conductivity measurements to ascertain how efficient the existence of H-
bond in a cobalt phosphinate structure may be in establishing proton conduction pathways. The corresponding Nyquist plots for the parent phosphinic acid and compound 3, at different temperatures and 95% RH are shown in Figure S5 and the Arrhenius plots are given in Figure S6. As can be seen, the formation of cobalt coordination polymers lowers the proton conductivity with respect to the phosphinic acid (σ ~ 7·10⁻⁵ S·cm⁻¹ at 70 °C and 95% RH) dropping up to 2·10⁻⁶ S·cm⁻¹ for the cobalt derivative. Post-impedance analyses (TG curves and powder X-ray diffractions, Figures S7 and S8, respectively), revealed no changes under measurement conditions. The Eₐ values, lower than 0.4 eV, indicated a Grotthuss-type mechanism. The low proton conductivity of cobalt phosphinate is attributed to isolation of the hydrophilic regions by phenyl groups that impede creating favorable extended proton conduction pathways.

To evaluate the electrocatalytic properties, solids 3 and 4, we have conducted different thermal treatments and analyzed the corresponding thermal decomposition products by PXRD and XPS. In comparison with compounds 1 and 2, which exhibit weight losses in the TG curves, associated to decarboxylation and combustion of the organic moiety (Figure 3) before formation of the corresponding metal pyrophosphates, at 900 °C in air; cobalt compounds are characterized not only by the loss of water in two different stages (compound 3), but also because the final decomposition products, at 900 °C, are compositionally distinct. Compound 3, both in air and N₂ (Figure 3), shows two initial consecutive weight losses between RT and 200 °C. The first one due to the removal of one of the lattice water at 100 °C (calculated weight loss 2.93%, observed 2.74%) and a second corresponding to the elimination of the second lattice water together with the coordinated water molecules. The total weight loss observed at 200 °C, 11.20%, agrees well with the calculated, 11.72%. The resulting poorly crystalline anhydrous phase is stable up to 300 °C and fully recovers lattice water and crystallinity by exposure of the sample at 95% RH for 3 days (Figure S8). Complete thermal decomposition of 3 in air leads to the formation of the monoclinic Co₃P₂O₇ (PDF 01-084-2126, 3@900_O₂) at 900 °C (Figure S9), whereas solid 4 decomposed, at the same temperature, in Co₃(PO₄)₂ (PDF 00-013-0503, 4@900_O₂) (Table 2, Figure S10).

Under N₂, the thermal decomposition of 3 and 4 leads to different products. Thus, solid 3 decomposes between 360 and 600 °C giving Co₃P₂O₇ (3@600_N₂), which transforms, between 740 and 900 °C, to Co₃P (PDF 01-089-3030, 3@1000_N₂), as unique crystalline phase. Compound 4 experiences a transformation, between 400 and 600 °C, to an amorphous material, stable up to 700 °C, that further decomposes to Co₃P (PDF 01-089-3030, 4@1000_N₂), at 1000 °C (Table 2, Figure S10).

![Figure 3. Thermogravimetric analyses in air (solid lines) and N₂ (dot lines) for 1 (black line), 2 (blue line), 3 (green line) and 4 (purple line).](image)

![Figure 4. XPS of P 2p (left) and Co 2p₃/2 (right) regions for pyrolyzed cobalt derivatives in N₂ at different temperatures.](image)
phase. In addition, the P 2p region shows a broad peak (134.2 eV), which is characteristic of P(V) in cobalt pyrophosphate for 4@600_N2. However, for the 1000 °C-pyrolyzed samples, two additional bands appear, at 130.7 eV and 129.8 eV, corresponding to phosphide ions bonded to Co2+. The morphology of the samples was studied by scanning electron microscopy (SEM). Figure 5 shows SEM images for 3 and 4, as well as for the corresponding pyrolyzed derivatives. For solid 3, the as-prepared precursor presents a fibrous-like structure, with an average length of 5 µm, both, as single particles and bigger agglomerated particles. Such an agglomeration is more evident for the 200 °C-heated sample, treated in N2. Upon pyrolysis at 600 °C, the sample adopts a more sheet-like morphology, while at 1000 °C globular particles are apparent. In the case of compound 4, Figure 6, both precursor and 600 °C-pyrolyzed sample, exhibit a layered habit, although pyrolysis leads to size-decreased particles. At 1000 °C, compound 4, calcined in N2, is morphologically composed of small irregular (< 1 µm) particles that agglomerate in bigger aggregates.

![Figure 5. SEM images of 3 as: (a) as-synthesized, (b) 200 °C-heated, (c) pyrolyzed at 600 °C and (d) pyrolyzed at 1000 °C.](image)

![Figure 6. SEM micrographs of 4 as: (a) as-synthesized, (b) pyrolyzed at 600 °C and (c) pyrolyzed at 1000 °C.](image)
In order to further explore the electrocatalytic properties of cobalt derivatives, against the oxygen evolution reaction, LSV curves and Tafel plots were determined. The overpotential values and the corresponding Tafel slopes are given in Table 2 and Figure 7.

Table 2. Phases, overpotential, Tafel slope and TOF values for compounds 3, 4 and pyrolyzed derivatives.

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>Phase</th>
<th>Overpotential (mV)</th>
<th>Tafel slope (mV·dec⁻¹)</th>
<th>TOF (s⁻¹) (400 mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>as-synthesized</td>
<td>351</td>
<td>58.5</td>
<td>0.056</td>
</tr>
<tr>
<td>4</td>
<td>as-synthesized</td>
<td>351</td>
<td>60.3</td>
<td>0.064</td>
</tr>
<tr>
<td>3@900_O₂</td>
<td>Co₃P₂O₇</td>
<td>371</td>
<td>107.4</td>
<td>0.011</td>
</tr>
<tr>
<td>4@900_O₂</td>
<td>Co₂(PO₄)₂</td>
<td>372</td>
<td>108.7</td>
<td>0.010</td>
</tr>
<tr>
<td>3@200_N₂</td>
<td>3-anhydrous</td>
<td>339</td>
<td>51.7</td>
<td>0.076</td>
</tr>
<tr>
<td>4@200_N₂</td>
<td>4</td>
<td>348</td>
<td>58.3</td>
<td>0.068</td>
</tr>
<tr>
<td>3@600_N₂</td>
<td>Co₃P₂O₇</td>
<td>382</td>
<td>60.8</td>
<td>0.028</td>
</tr>
<tr>
<td>3@1000_N₂</td>
<td>Co₃P</td>
<td>369</td>
<td>58.3</td>
<td>0.028</td>
</tr>
<tr>
<td>4@1000_N₂</td>
<td>Co₃P</td>
<td>372</td>
<td>53.5</td>
<td>0.035</td>
</tr>
</tbody>
</table>

The best OER performance in alkaline solution, is shown by 3@200_N₂ (phase 3-anhydrous). This electrocatalyst requires an overpotential of 339 mV, at a current density of 10 mA·cm⁻², and a lower Tafel slope, 51.7 mV·dec⁻¹, which reveals a more favorable reaction kinetic toward the OER than that of the as-synthesized compound. Although 3@200_N₂ may be similarly hydrated as the corresponding as-synthesized material, it apparently exhibits higher accessibility of the metal sites presumably by a combined effect of dehydration/rehydration and the surface loss of the ligand upon reaction (see below, Table S3). On the other hand, 4@200_N₂ does not exhibit improved electrocatalytic properties in comparison to the as-synthesized precursor (4), probably because the latter compound remains essentially the same upon heating at 200 °C (Figure 3). For the remaining solids, both as-synthesized and pyrolyzed derivatives, show slightly higher overpotential values, around 351 mV for the precursors, and close to 370 mV for Co₃P₂O₇ and/or Co₃P phases. In addition, the Tafel slopes also experiences a slight increase, excepting for 900 °C-calcined samples in air, which displayed the highest values, around 107-108 mV·dec⁻¹. For the latter compounds, the very low site accessibility might be associated to a high degree of particle agglomeration, as observed by SEM. Interestingly, the overpotential and Tafel slope determined for 3@200_N₂ compares well with those values found for another morphologically different Co₃P₂O₇ compound (359 mV and 54.1 mV·dec⁻¹),⁴⁄金属 phosphonates¹⁸ or Co²⁺ pyrophosphates supported on different carbonaceous materials.²⁴, ⁴¹-⁴³ Calculated TOF values (Table 2), in the range 0.010 – 0.076 s⁻¹, are of the order of those reported for other Co(II)-MOFs.²⁸, ⁴⁴-⁴⁵ Figure S11 displays the Nyquist plots from the EIS measurements for the studied materials. It shows well-defined semicircles for all solids. 3@200C_N₂ displays the smallest semicircular diameter (Rₑ = 14.4 Ω), revealing the best OER performance for this material.

Preliminary studies to evaluate the electrocatalytic activity toward the ORR were carried out. The results indicate that the solids shown a low catalytic capability (Figure S12) toward oxygen reduction. The onset potentials (E onset) and halfwave potential (E₁/₂) obtained from the LSV curves are far from those obtained for Pt/C benchmark (1.01 V and 0.90 V, respectively), being 3@1000_N₂ the solid with the best behavior (0.79 V and 0.66 V, respectively).

Figure 7. (a) LSV curves and (b) Tafel slopes for solids 3, 4 and their pyrolytic products.

XPS analysis (Table S3), before and after OER and ORR tests, indicate that thermal treatments below 600 °C entail the surface loss of phosphorus (Table S3) due to hydrolysis in...
alkaline solution.\textsuperscript{41,46,47} On the other hand, the PXRD data (Figure S13) for solids calcined at 1000 °C show that the loss of phosphide, as revealed by XPS (Figure S14), is only superficial, since Co\textsubscript{2}P is still present as the only crystalline phase after conducting the electrocatalytic tests.

Conclusions

While the structures of Ca\textsuperscript{2+} and Cd\textsuperscript{2+} (2-carboxyethyl)(phenyl)phosphinates follow the usual patterns of crystallization of related compounds, i.e. a layered topology of isolated metal octahedra, with interdigitated phenyl groups pointing to the interlayer space, the Co\textsuperscript{2+} derivative presents a characteristic 1D topology, of edge-sharing metal octahedra in zig-zag arrangement. Although H-bond interactions are established with the participation of water molecules and the ligand hydrophilic groups, the solid presents low proton conductivity attributed to the lack of extended H-bond network. Zirconium pyrophosphates/phosphates, whereas in N\textsubscript{2}, crystalline Co\textsubscript{2}P form at 1000 °C. Preliminary results indicate that, for OER, the pyrolyzed cobalt derivatives present a moderate activity comparable to other related material, but it could not be attributed to any specific Co\textsuperscript{2+} chemical environment.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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