Preparation and Properties of Proton Conductors and HER Electrocatalysts Based on Multifunctional Transition Metal Sulfophosphonates

Á. Vílchez-Cózar[1,2]*, I.R. Salcedo[3], K. Xanthopoulos[4], R. M. P. Colodrero[1,2], M. Bazaga-García[1,2], K. D. Demadis[4], P. Olivera-Pastor[1,2] and A. Cabeza[1,2]

[1] Department of Inorganic Chemistry, Crystallography and Mineralogy. University of Málaga. Spain.
[2] Instituto Universitario de Investigación de Nanomateriales y Tecnología (IMANA). University of Málaga. Spain.
[3] Servicios Centrales de Apoyo a la Investigación (SCAI). University of Málaga. Spain..
[4] Department of Chemistry. University of Crete. Greece.

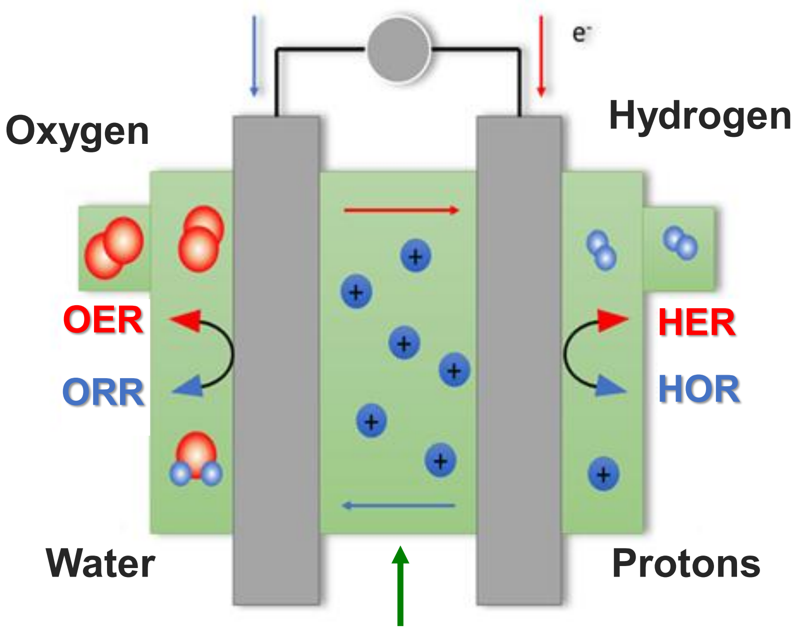
*vilchez@uma.es

Index

1. **Introduction**
   - Energy Conversion Devices
   - Electrocatalyst Precursors
2. **Synthesis and Crystal Structures**
   - Derivatives with Mn^{2+}, Fe^{2+} and Co^{2+}
   - Derivatives with Zn^{2+}
3. **Proton Conductivity**
4. **Electrocatalysis**
5. **Conclusions**

Energy-conversion Devices

- Addressing current **energy challenges**
- Developing low-cost and efficient **electrolytes** and **electrodes** for low-temperature **fuel cells** and **electrolyzers**
- **Metal sulfophosphonates**: versatile hybrid materials
  - ✓ High proton conductivity (-PO_3H_2 & -SO_3H acidic groups): **Proton Exchange Membrane**
  - ✓ Precursors of **highly active P-containing Electrodes**



Proton Exchange Membrane

- Key electrocatalytic reactions in energy storage and conversion systems

Reaction			Current Catalysts
HER	Hydrogen Evolution Reaction	$H^+ + e^- \rightarrow ½ H_2$	Pt, Pd
OER	Oxygen Evolution Reaction	$O^{2-} \rightarrow ½ O_2 + 2e^-$	RuO_2, IrO_2
HOR	Hydrogen Oxidation Reaction	$½ H_2 \rightarrow H^+ + e^-$	Pt, Pd
ORR	Oxygen Reduction Reaction	$½ O_2 + 2e^- \rightarrow O^{2-}$	Pt, Pd

- **Nafion®**: Common electrolyte in PEMFCs
  - ✓ **$\sigma \sim 10^{-1} – 10^{-2}$ S·cm^{-2} at 80 ºC and 98% RH**
  - ✗ **σ ↓↓ at T > 85 ºC and RH < 98%**

Electrocatalyst Precursors

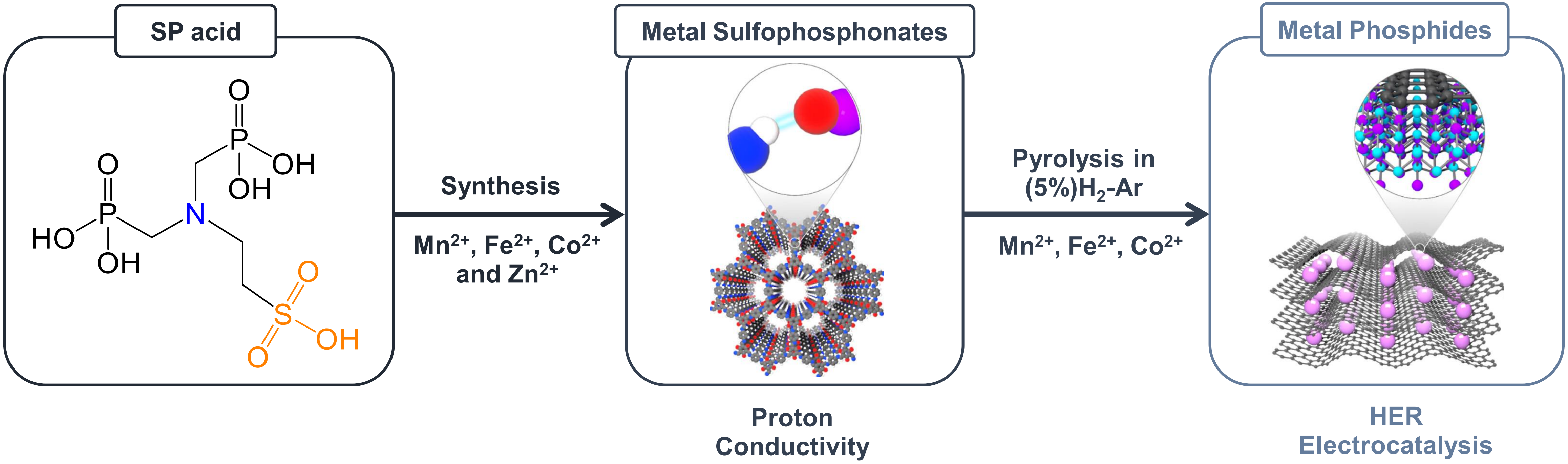
- **Metal phosphonates** as promising **precursors** to **P-containing electrocatalysts**: metal phosphides, phosphates and polyphosphates

  ✓ Rich **coordination chemistry** (Mn, Fe, Co, Ni)

  ✓ **Heteroatoms (N,S)** sources and carbon substrate: organic linkers

  ✓ Uniformly dispersion of the **metal sites**

  ✓ **Catalytic performance** improved by several addition strategies (rGO, CNTs…)



Derivatives with Mn^{2+}, Fe^{2+} and Co^{2+}

➢ Synthesis of $M_2[(O_3PCH_2)_2NH(CH_2)_2SO_3)(H_2O)_3]$ (M_2SP-3)

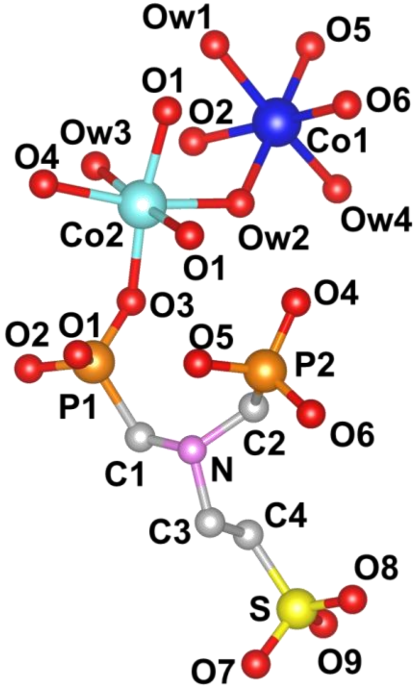
Compound	M:L molar ratio	H_2O:solvent (mL)
Mn_2SP-3	1.788:1.277	6:3.6 (EtOH)
Fe_2SP-3	0.708:0.354	2:1.9 (iPrOH)
Co_2SP-3	0.708:0.354	4:3.8 (iPrOH)

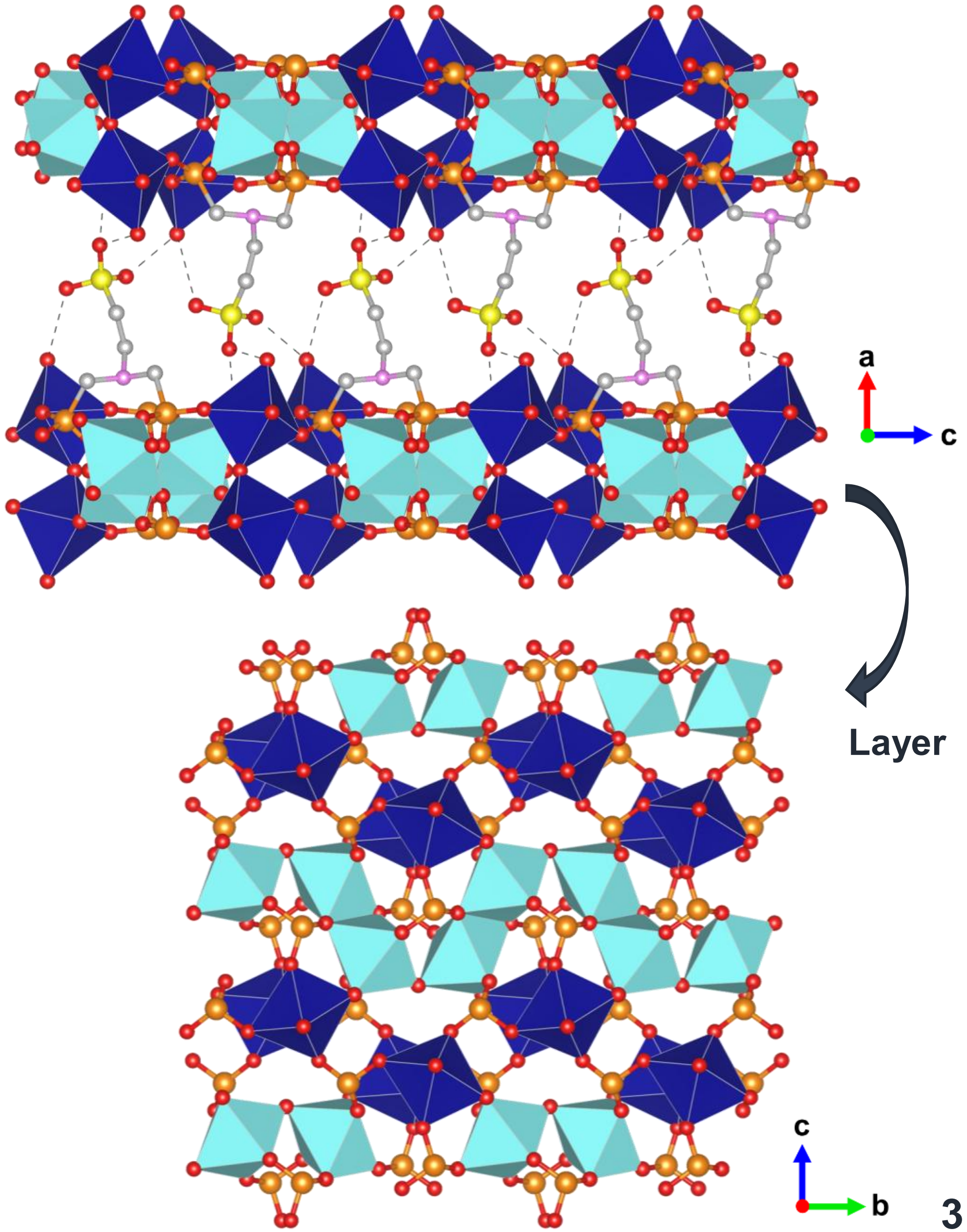
MW, 160 ºC → 1 hour

➢ Crystal Structure

Crystallographic data from XRPD data

Compounds	Mn_2SP-3	Fe_2SP-3	Co_2SP-3
Space Group	*Pcnb*	*Pcnb*	*Pcnb*
λ (Å)	0.6198	0.7093	0.7093
a (Å)	26.5105(3)	26.321(4)	26.3863(9)
b (Å)	10.3727(7)	10.2485(1)	10.1457(3)
c (Å)	10.0305(7)	9.8989(1)	9.8448(3)
α, β, γ (°)	90.0	90.0	90.0
V (Å³)	2758.22(5)	2670.2(7)	2635.52(1)
Z	8	8	8
R_{WP} (%)	3.52	3.96	4.17
R_P (%)	2.3	3.05	3.25
R_F (%)	2.49	5.21	2.88





Synthesis Conditions and Chemical Composition of Zn^{2+} derivatives

High-throughput Methodology

Synthesis Approach
- Hydrothermal
- Reflux

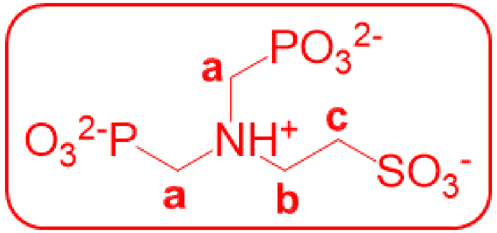
Synthesis Parameters
- M:L molar ratio
- Ligand source
- Solvent(s)
- Temperature
- Reaction time

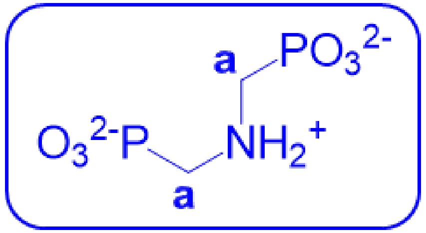
	Molecular Formula	Acronyms	Dimensionality
	Hydrothermal synthesis (150 °C)		
1	$Zn_{2.33}H_{0.34}\{[(O_3PCH_2)_2N(CH_2)_2SO_3)](H_2O)_3]\cdot 4H_2O$	**$Zn_{2.33}$SP-7**	3D[1,2]
2	$(NH_4)Zn_2[(O_3PCH_2)_2N(CH_2)_2SO_3]$	**$(NH_4)Zn_2$SP-0**	2D[2]
3	$NaZn_3H[(O_3PCH_2)_2NH(CH_2)_2SO_3]_2\cdot 5H_2O$	**$NaZn_3SP_2$-5**	Amorphous
4	$(NH_4)_2Zn_3\{[(O_3PCH_2)_2NH(CH_2)_2SO_3][(O_3PCH_2)_2NH]\}\cdot 3H_2O$	**$(NH_4)_2Zn_3$SP-IP-3**	2D[2]
5	$NaZn_3\{[(O_3PCH_2)_2NH(CH_2)_2SO_3][(O_3PCH_2)_2NH_2](H_2O)_4\}\cdot H_2O$	**$NaZn_3$SP-IP-5**	2D[2]
6	$Zn_3[(O_3PCH_2)_2NH_2]_2$	**Zn_3IP_2-0**	3D[2]
	Reflux synthesis		
7	$Zn_2\{[(O_3PCH_2)_2NH(CH_2)_2SO_3](H_2O)_2\}$	**Zn_2SP-2**	2D[3]
8	$(NH_4)Zn_2\{[(O_3PCH_2)_2N(CH_2)_2SO_3](H_2O)\}\cdot H_2O$	**$(NH_4)Zn_2$SP-2**	2D[2]

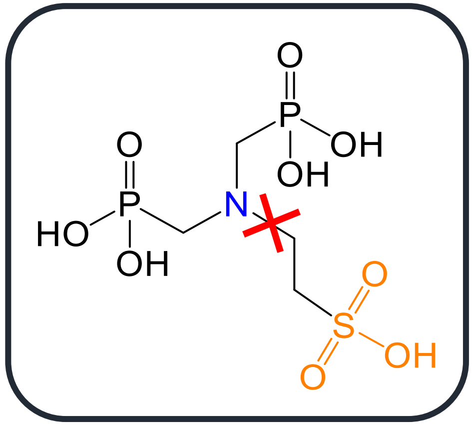
1: 3D Electron Diffraction; **2**: SXRPD; **3**: LXRPD

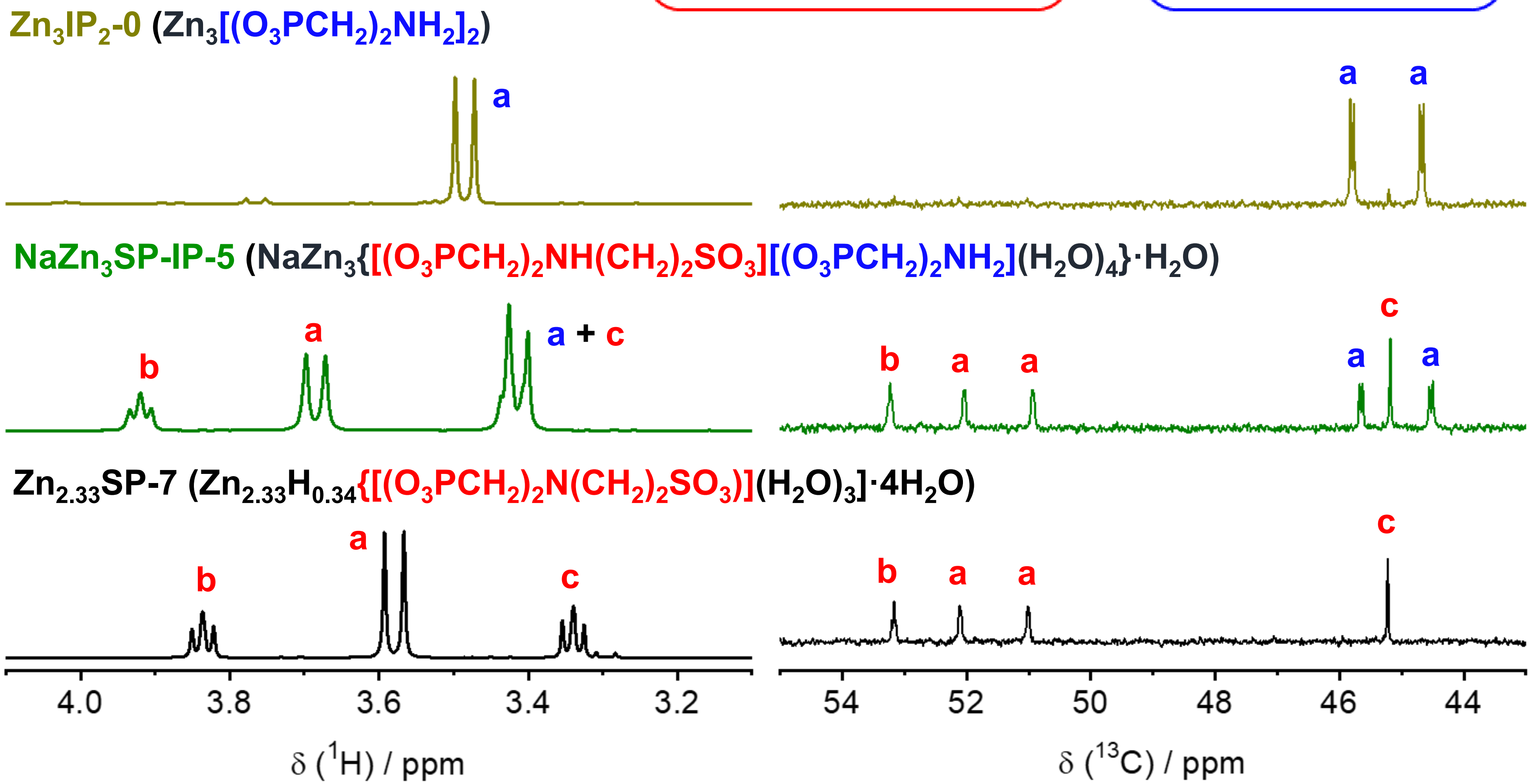
Derivatives with Zn^{2+}

➢ **Study of the Ligand Fragmentation by Liquid ^{1}H and ^{13}C NMR**









Iminodimethylphosphonate ligand (IP)

Mixture SP + IP

2-[Bis(phosphonomethyl)amino]-ethanesulfonate ligand (SP)

Derivatives with Zn^{2+}

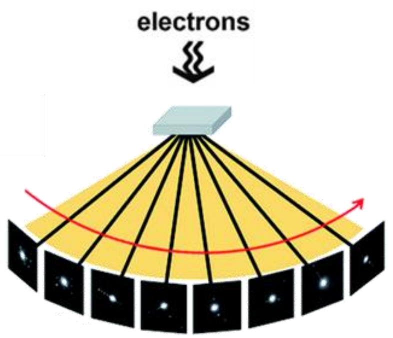
- **Crystal Structure of $Zn_{2.33}$SP-7:** $Zn_{2.33}H_{0.34}\{[(O_3PCH_2)_2N(CH_2)_2SO_3)](H_2O)_3\}\cdot 4H_2O$

Le Bail fit (SXRPD)	
Crystal System	Hexagonal
Space Group	P-3*c*1
λ (Å)	0.6197
a, b (Å)	27.1601(6)
c (Å)	9.2215(2)
V (Å^3)	**5891.1(3)**
R_{WP} (%)	5.71
R_P (%)	3.84

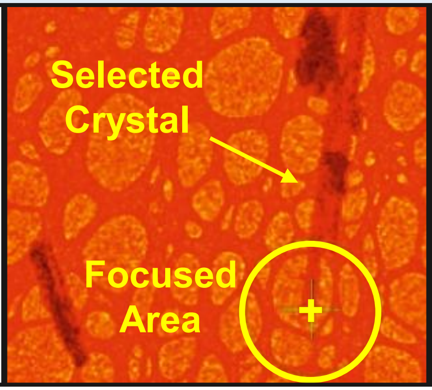
Structure Resolution ✗

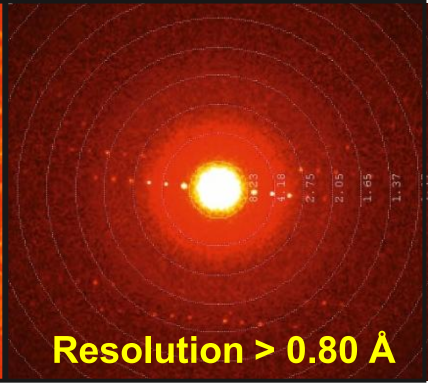
✓ →

3D Electron Diffraction



Selected Measurement Conditions:
Electron source: 200 kV
Temperature: 100 K
Exposure time (0.5s/º)
[from -64º to +63.75º]

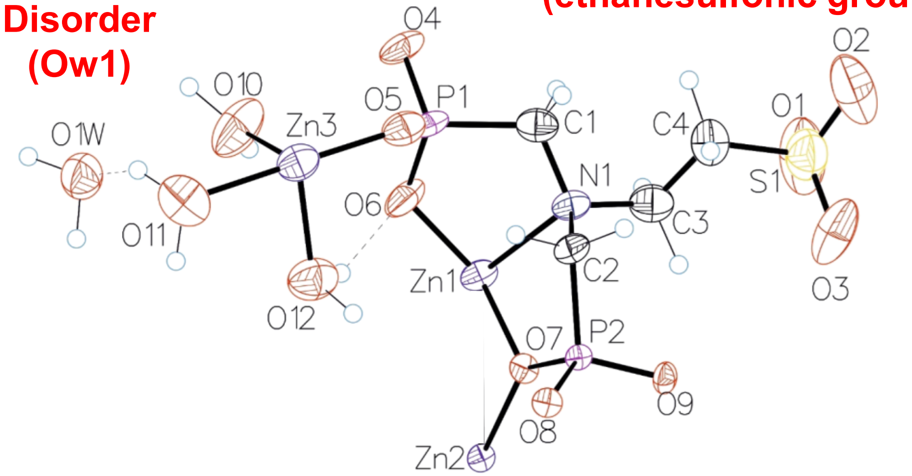


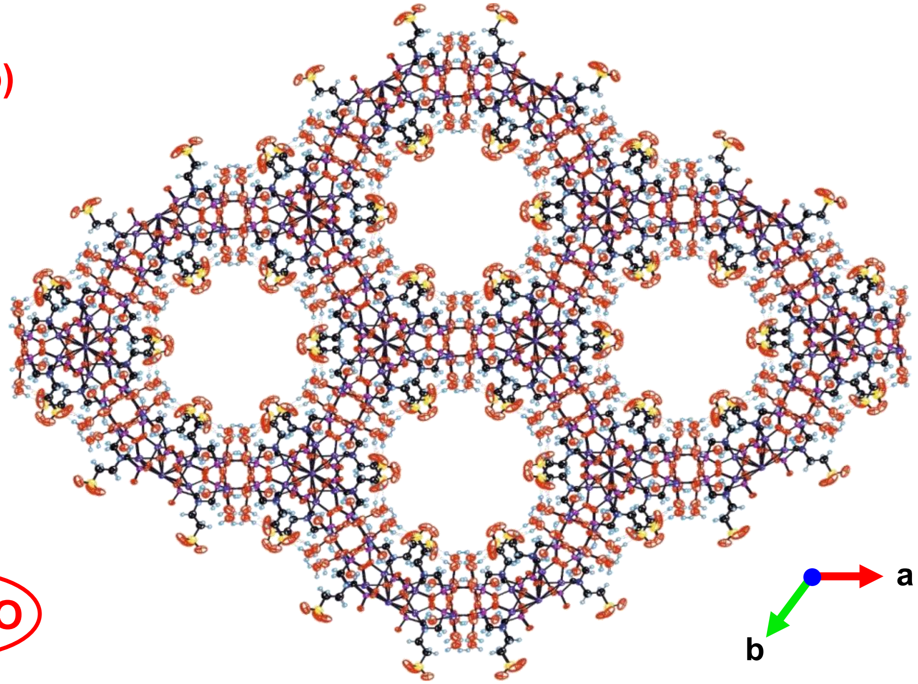


3D Electron Diffraction	
Crystal System	Hexagonal
Space Group	P-3*c*1
a, b (Å)	26.715(3)
c (Å)	9.1625(6)
V (Å^3)	**5663.1(10)**
F^2	1.170
R_1 (all data)	0.1923
R_2 (all data)	0.3933

Disorder (Ow1)

Disorder (ethanesulfonic group)



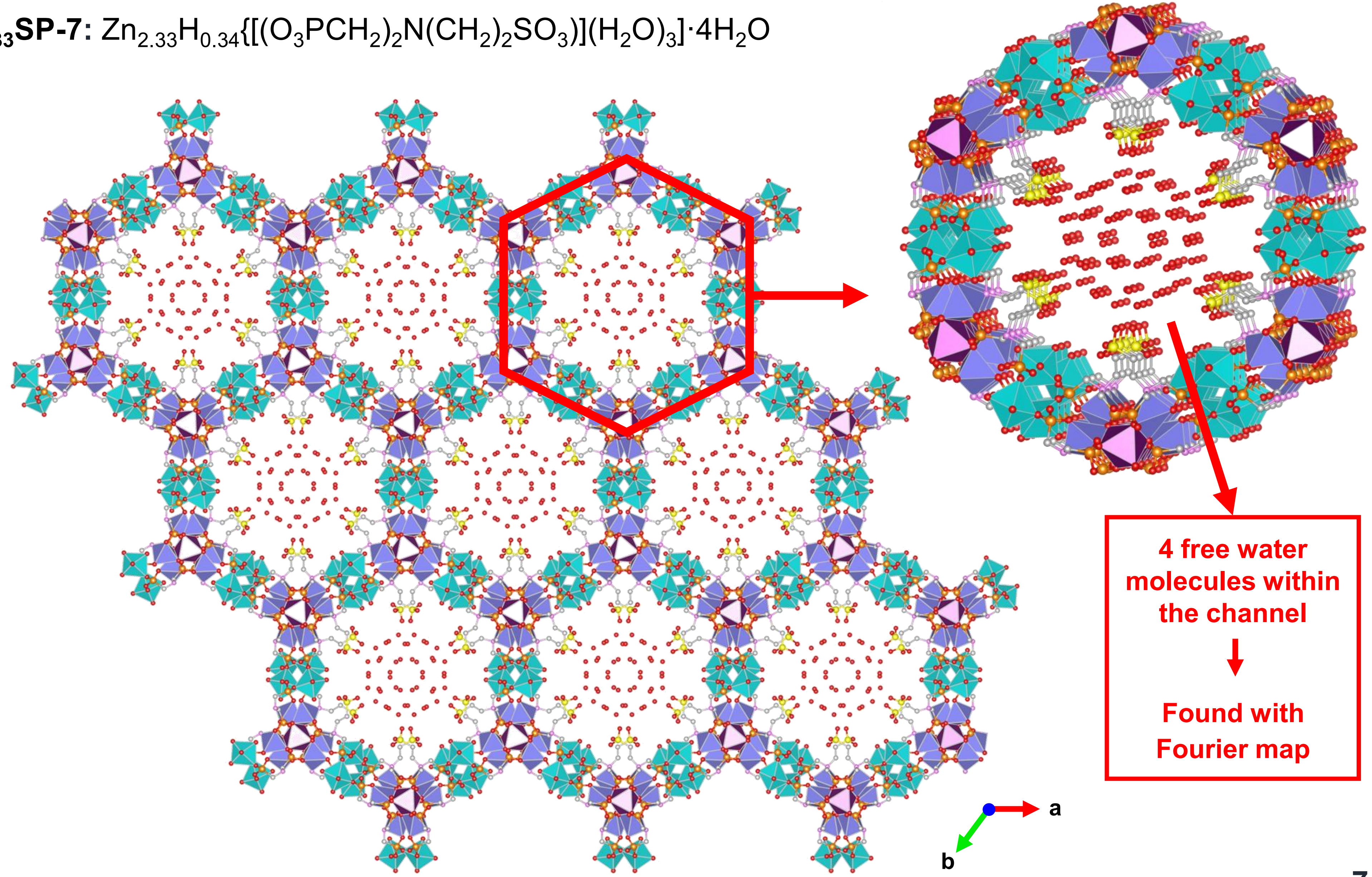


$Zn_{2.33}H_{0.34}\{[(O_3PCH_2)_2N(CH_2)_2SO_3)](H_2O)_3\}$**$\cdot 0.4H_2O$**
$Zn_{2.33}$SP-3.4

Derivatives with Zn^{2+}

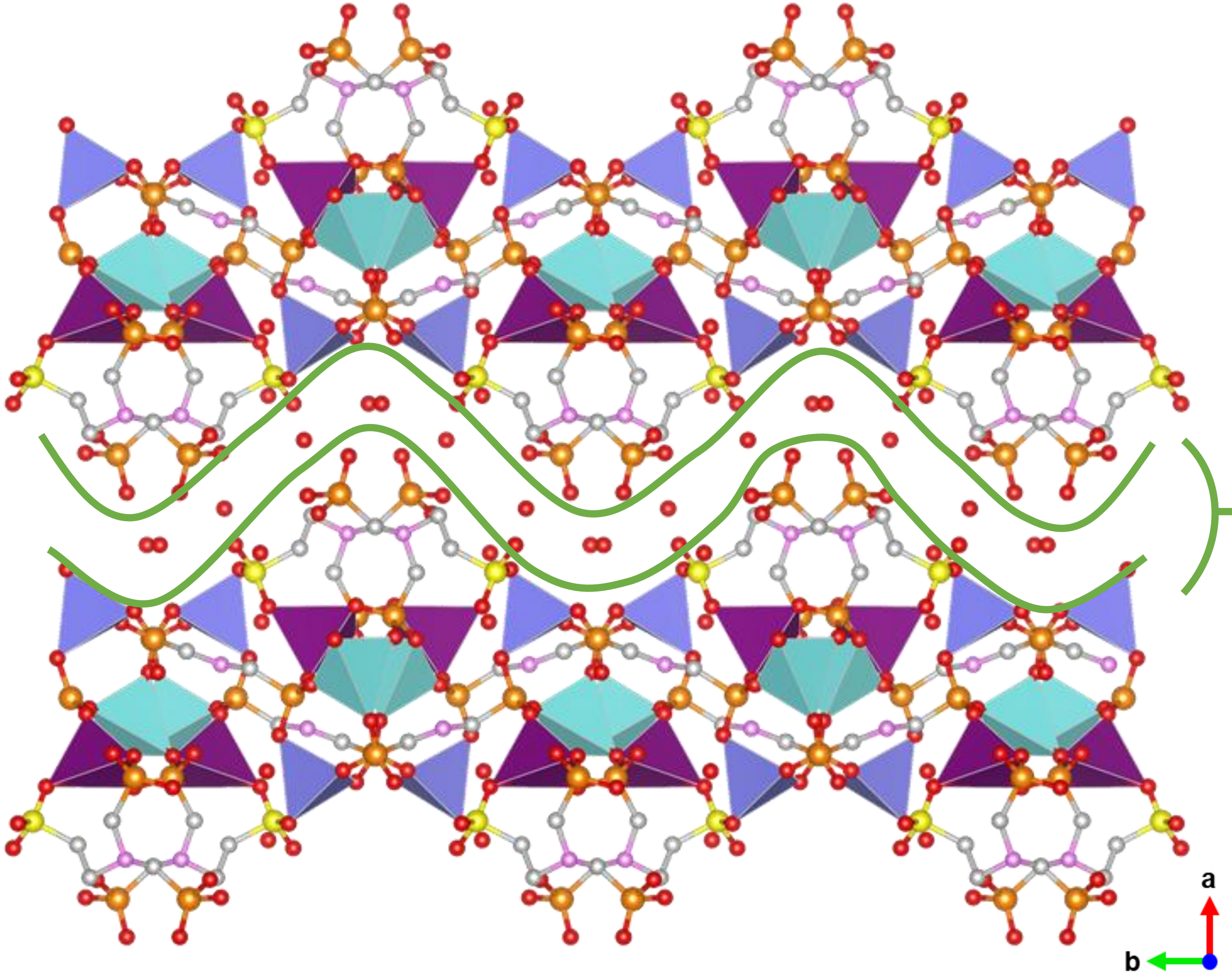
➢ **Crystal Structure of $Zn_{2.33}$SP-7**: $Zn_{2.33}H_{0.34}\{[(O_3PCH_2)_2N(CH_2)_2SO_3)](H_2O)_3]\cdot 4H_2O$

SXRPD	
Space Group	P-3*c*1
λ (Å)	0.6197
a (Å)	27.1890(29)
b (Å)	27.1890(29)
c (Å)	9.2122(4)
α (°)	90.0
β (°)	90.0
γ (°)	120.0
V (Å³)	**5897.7(8)**
Z	4
Range data (°)	1.2-50.0
Reflections	5244
Data	8108
Restrains	81
Parameters	141
R_{WP} (%)	6.79
R_P (%)	4.55
R_F (%)	5.38



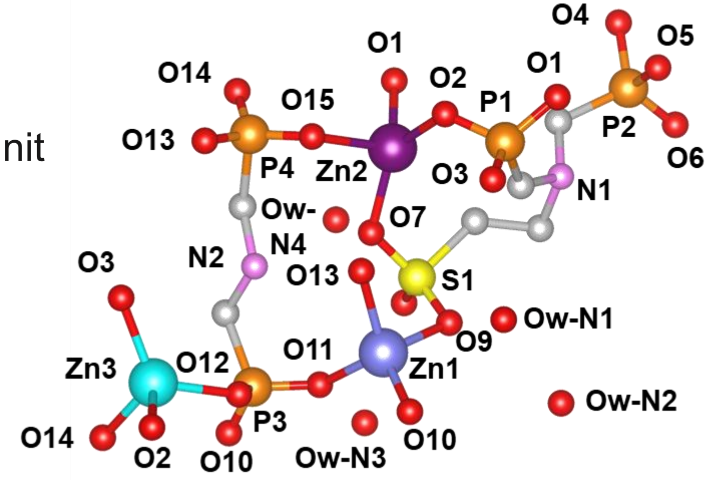
Derivatives with Zn^{2+}

➢ **Crystal Structure of $(NH_4)_2Zn_3$SP-IP-3:** $(NH_4)_2Zn_3\{[(O_3PCH_2)_2NH(CH_2)_2SO_3][(O_3PCH_2)_2NH]\}\cdot 3H_2O$

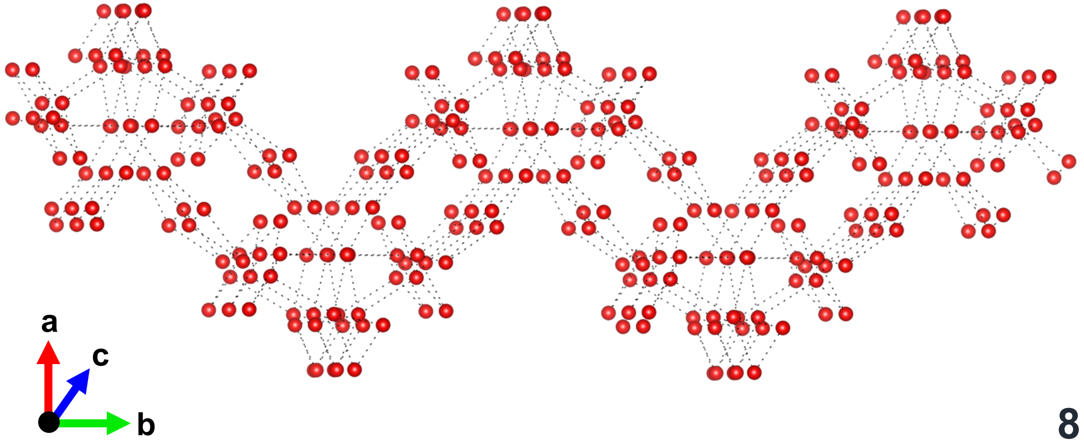


a: 16.5633(12) Å, *b*: 16.2522(7) Å, *c*: 9.52035(35) Å, ***β***: 101.062(4)°, **V**: 2515.18(23) Å^3

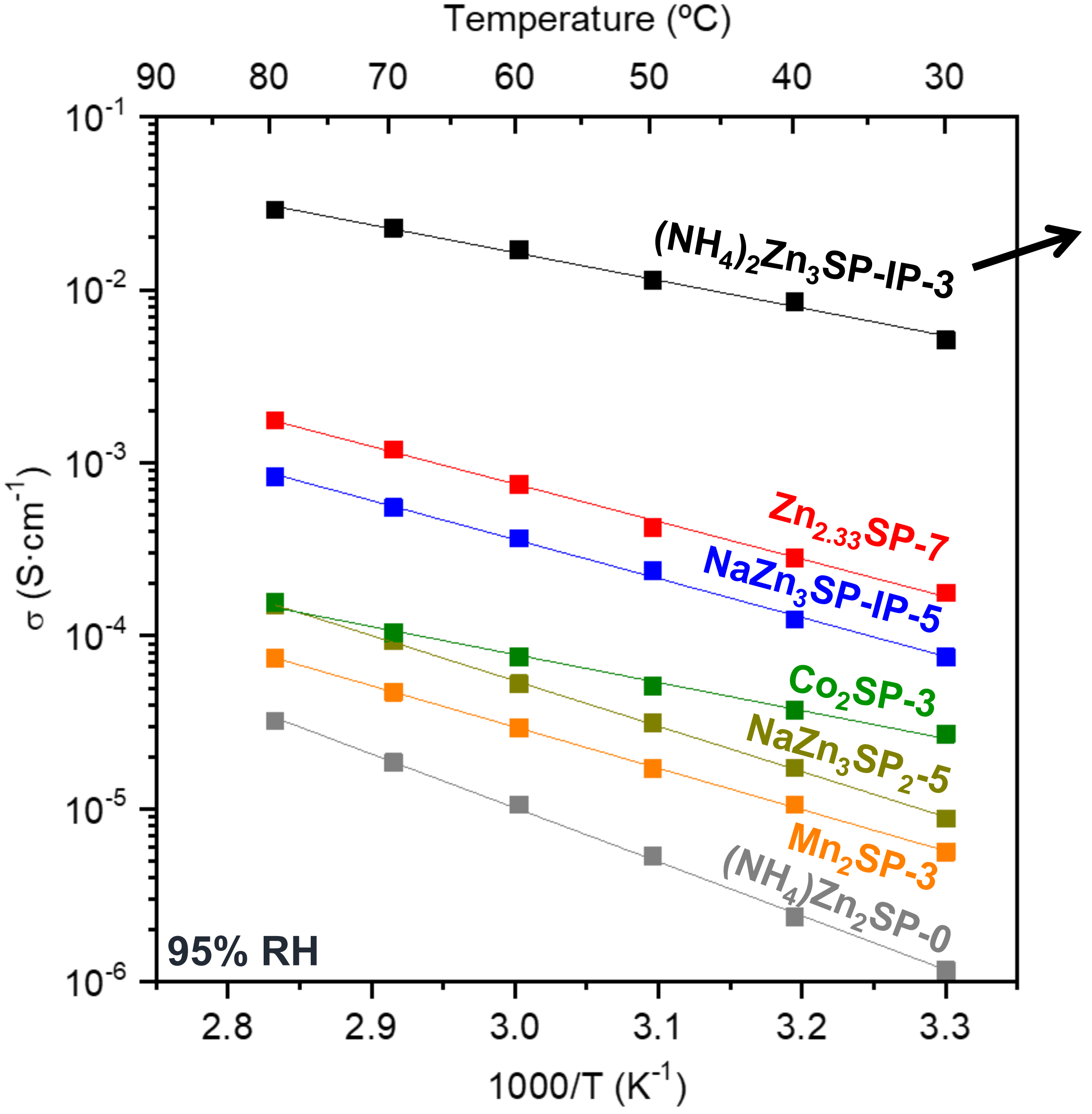
Extended assymetric unit

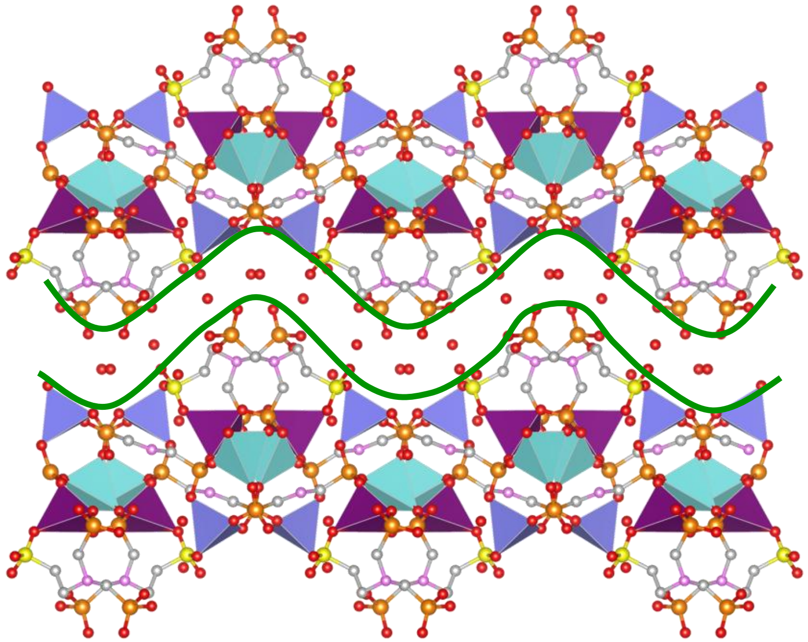


Interlayered unbound water molecules and $(NH_4)^+$ ions located from Fourier map



➢ Proton Conductivity Properties

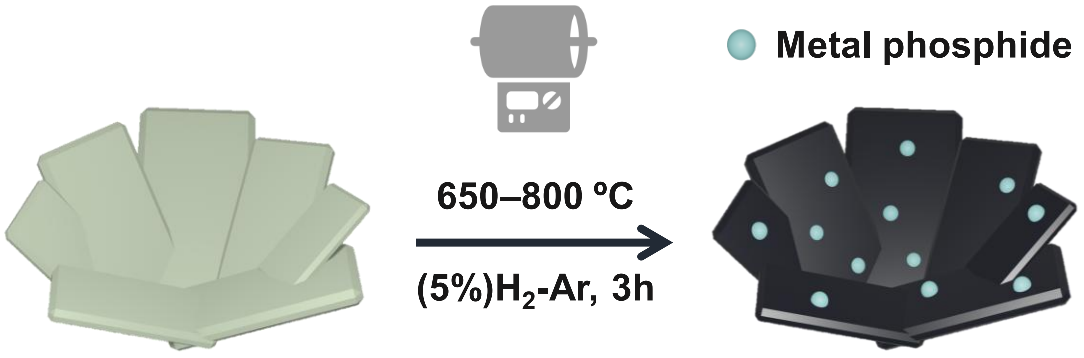




✓ Interlayered unbound water and $(NH_4)^+$ ions
↓
Extended H-bonding interactions

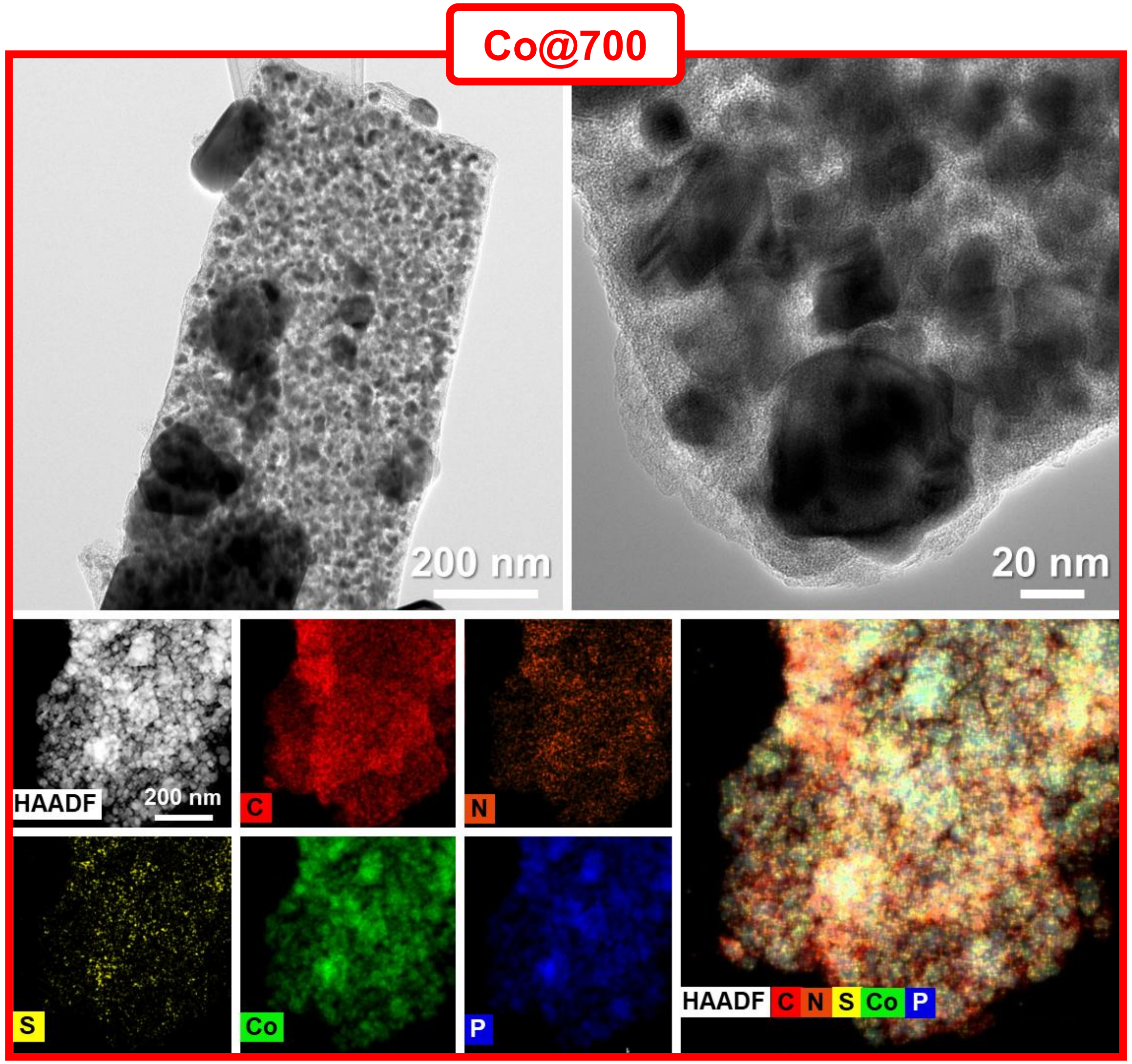
Sample		95% RH σ (S·cm^{-1})	95% RH E_a (eV)	75% RH σ (S·cm^{-1})	75% RH E_a (eV)
$(NH_4)_2Zn_3SP$-IP-3	2D	2.9×10^{-2}	0.32	5.4×10^{-4}	0.44
$Zn_{2.33}SP$-7	3D	1.8×10^{-3}	0.43	1.9×10^{-4}	0.36
$NaZn_3SP$-IP-5	---	8.4×10^{-4}	0.45	8.6×10^{-5}	0.49
Zn_3IP_2-0	3D	1.8×10^{-4}	0.43	8.5×10^{-6}	0.49
Co_2SP-3	2D	1.6×10^{-4}	0.33	2.1×10^{-6}	0.39
$NaZn_3SP_2$-5	2D	1.4×10^{-4}	0.52	5.5×10^{-6}	0.51
Mn_2SP-3	2D	7.5×10^{-5}	0.46	1.1×10^{-6}	0.38
Fe_2SP-3	2D	3.9×10^{-5}	0.44	5.7×10^{-6}	0.39
$(NH_4)Zn_2SP$-0	2D	3.2×10^{-5}	0.62	3.2×10^{-7}	0.72
$(NH_4)Zn_2SP$-2	2D	3.0×10^{-6}	0.65	---	---
Zn_2SP-2	2D	1.9×10^{-6}	0.64	---	---

➤ Preparation of Metal Phosphides (M_xP) by Pyrolysis in (5%)H_2-Ar atmosphere



Metal Sulfophosphonate (M= Mn^{2+}, Fe^{2+}, Co^{2+})

N,S-doped carbon/ M_xP catalyst

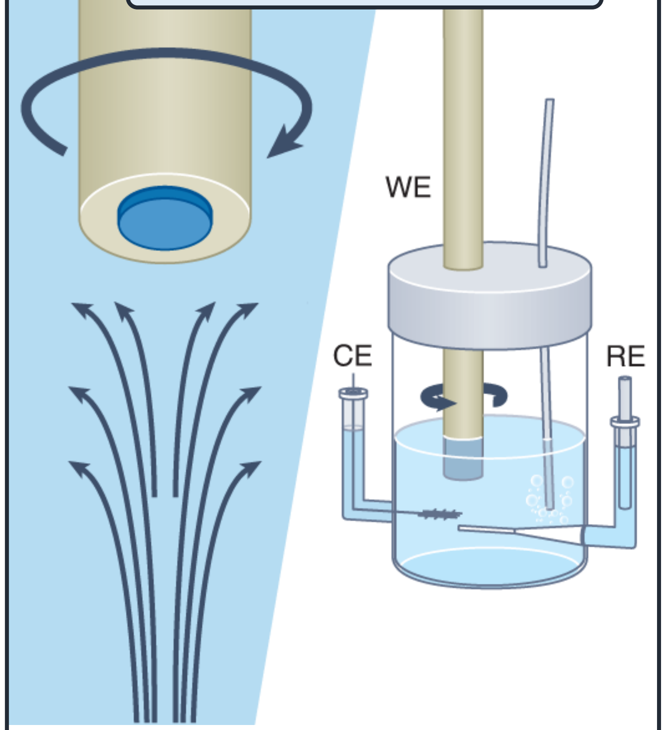


Phase identification and elemental analysis

Catalysts	Crystalline phases	C (wt.%)	N (wt.%)	S (wt.%)
Mn@800	*m*-$Mn_2P_2O_7$	9.00	0.34	0.04
Fe@800	*a*-$Fe_2P_2O_7$ (31%) + *h*-Fe_2P (13%) + *o*-FeP (56%)	14.98	0.53	0.00
Co@700	***o*-CoP (81%) + *o*-Co_2P (19%)**	**12.35**	**0.76**	**0.14**

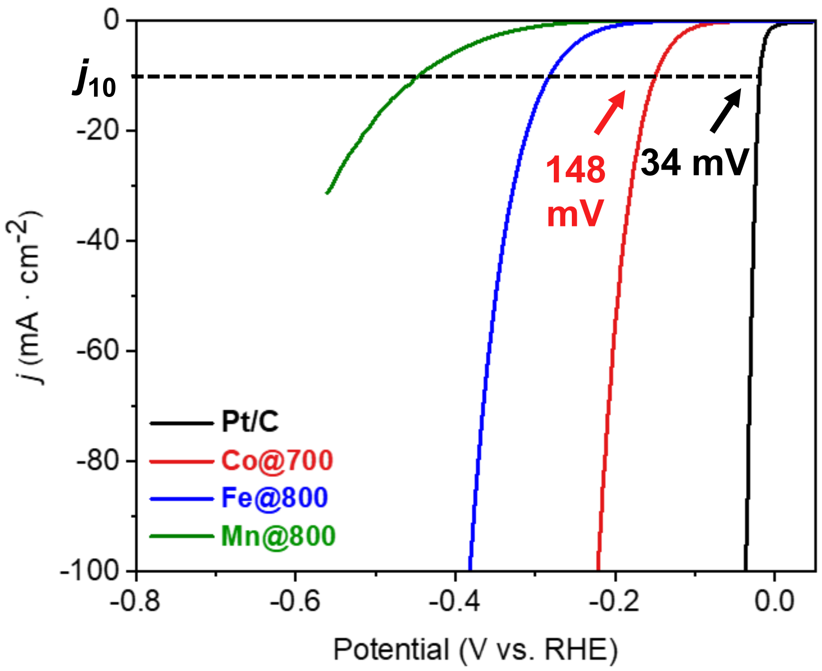
➢ Hydrogen Evolution Reaction (HER) Performance of Metal Phosphides

Three-electrode setup



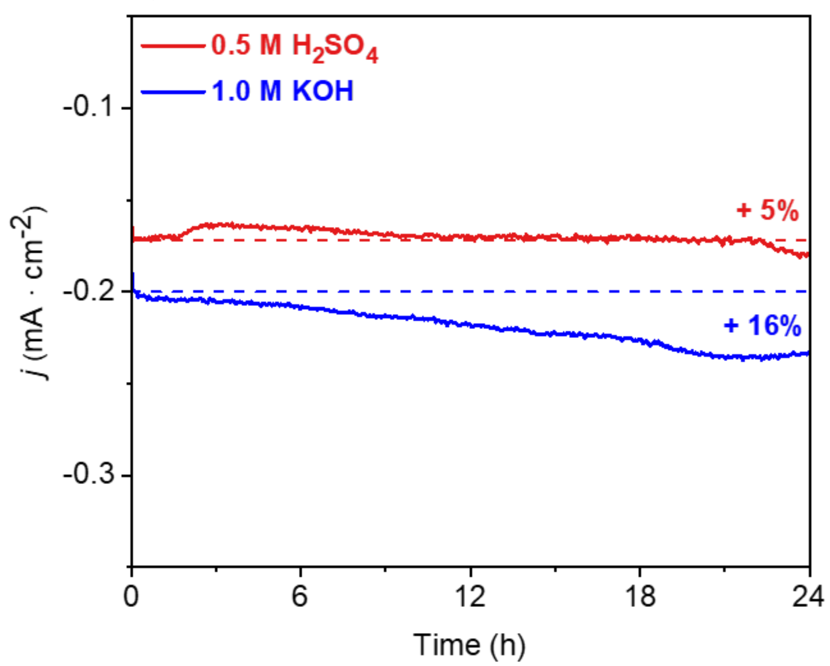
Working electrode:
Catalyst deposited on RDE or CFP
Reference electrode:
Ag/AgCl (3M KCl)
Counter electrode:
CFP

LSV curves (0.5 M H_2SO_4)



Co@700

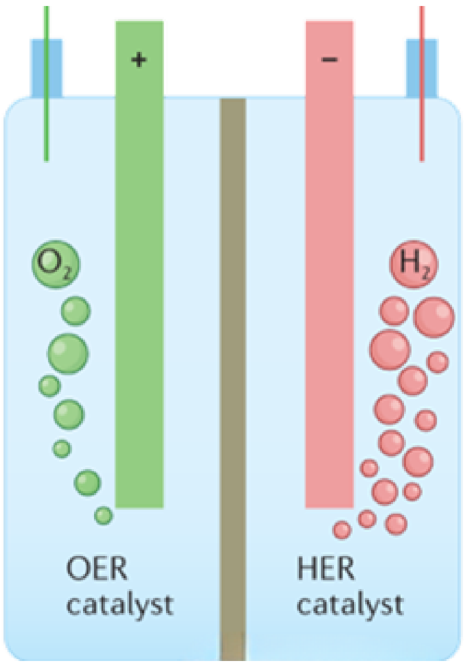
Stability tests @100 mA·cm^{-2}



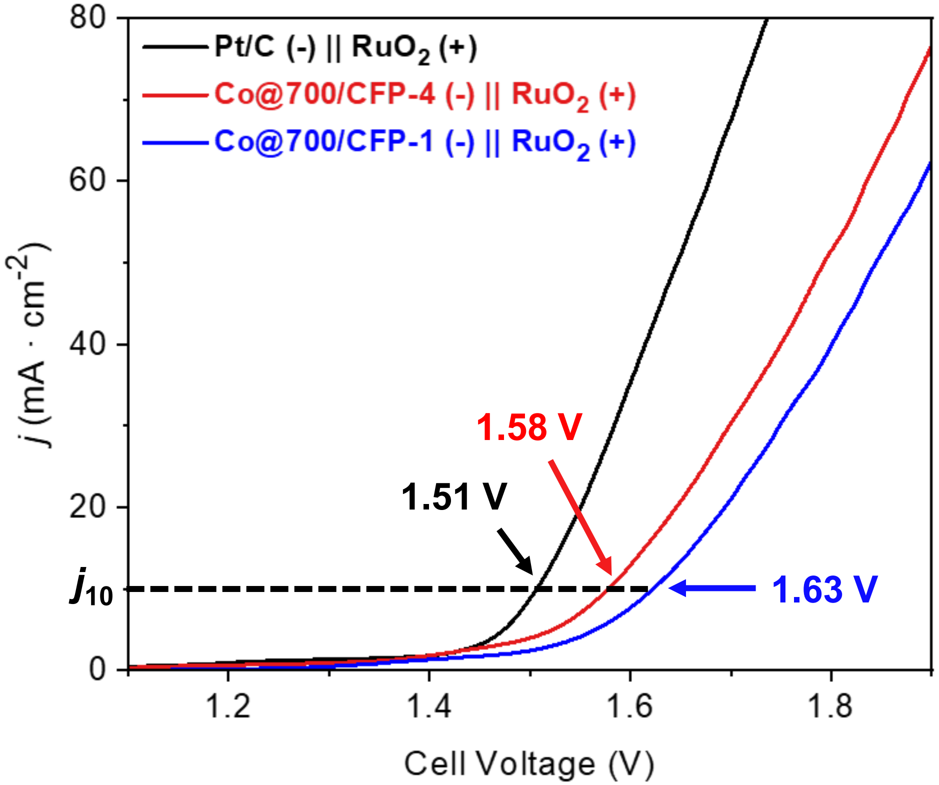
Catalyst	**Phase Composition** (wt.%)	η_{10} (mV)
Co@700	*o*-CoP (81%) + *o*-Co_2P (19%)	148
Fe@800	*a*-$Fe_2P_2O_7$ (31%) + *h*-Fe_2P (13%) + *o*-FeP (56%)	282
Mn@800	*m*-$Mn_2P_2O_7$	447

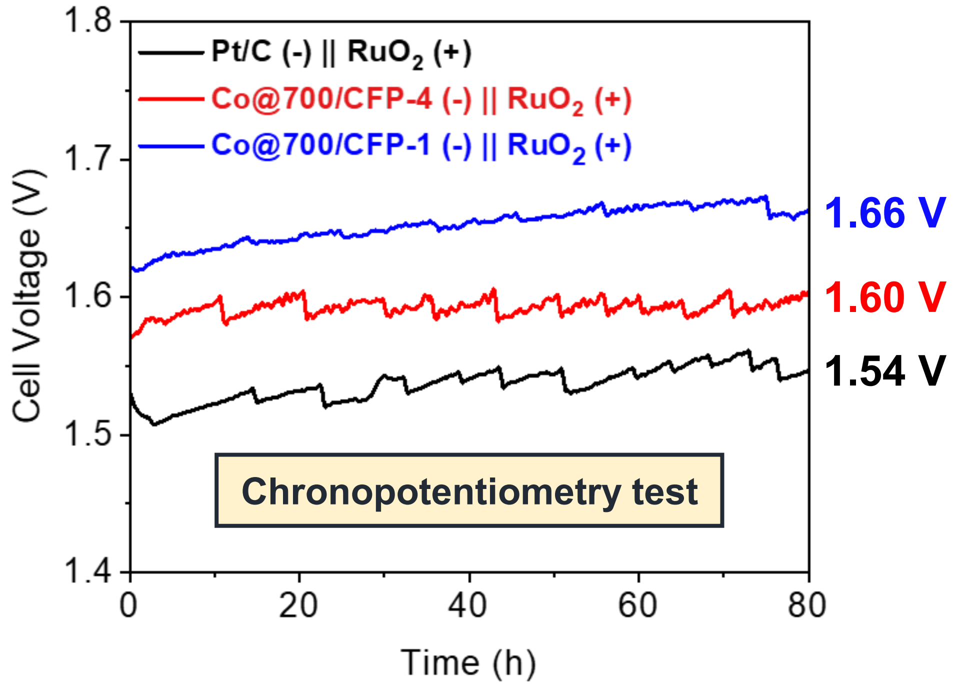
➢ Performance of Cobalt Phosphides in Alkaline Water Splitting (1.0 M KOH)

AWE system



Cathode (-): 20%-Pt/C
Anode (+): RuO_2 or Metal Pyrophosphate/Phosphide





System		Cathode loading (mg·cm^{-2})
Pt/C (-) || RuO_2 (+)	▬ (black)	1
Co@750-H_2 (-) || RuO_2 (+)	▬ (red)	4
Co@750-H_2 (-) || RuO_2 (+)	▬ (blue)	1

Conclusions

- A wide variety of divalent transition metal phosphonates (M = Mn^{2+}, Fe^{2+}, Co^{2+}, and Zn^{2+}) with the **2-[bis(phosphonomethyl)amino]-ethanesulfonate** ligand have been synthesized to evaluate their proton-conducting properties and their use as electrocatalyst precursors upon pyrolysis (Co^{2+}).

- Eleven new crystal structures were solved, using both **synchrotron/laboratory XRPD,** most of these compounds exhibit a layered structure with remarkable structural diversity, in part due to fragmentation of the ligand during reaction. Notably, the solid $Zn_{2.33}H_{0.34}\{[(O_3PCH_2)_2N(CH_2)_2SO_3)](H_2O)_3]\cdot 4H_2O$, exhibits a zeolitic-type structure, with a unit cell volume of ~ 6.000 $Å^3$, as determined by **3D electron diffraction**.

- The proton conductivity values for the studied compounds vary considerably in a wide range, with the 2D ammonium mixed ligand Zn derivative, **$(NH_4)_2Zn_3$SP-IP-3,** showing the highest proton conductivity ($3\cdot 10^{-2}$ $S\cdot cm^{-1}$ at 80ºC and 95% RH). This may be attributed to creation of extended H-bond networks, which facilitate easy proton transfer pathways through water-mediated Grotthuss-type mechanism.

- A cobalt sulfonate derivative pyrolyzed at 700 °C in 5%-H_2/Ar, composed of a mixture Co_2P and CoP phases, displayed a high HER activity (η_{10} = 148 mV in 0.5 M H_2SO_4) and remarkable stability.

Thank you for your attention

Preparation and Properties of Proton Conductors and HER Electrocatalysts Based on Multifunctional Transition Metal Sulfophosphonates

Á. Vílchez-Cózar, I.R. Salcedo, K. Xanthopoulos, R. M. P. Colodrero, M. Bazaga-García, K. D. Demadis, P. Olivera-Pastor and A. Cabeza

vilchez@uma.es

Department of Inorganic Chemistry, Crystallography and Mineralogy. University of Málaga. Spain.
Instituto Universitario de Investigación de Nanomateriales y Tecnología (IMANA). University of Málaga. Spain.
Servicios Centrales de Apoyo a la Investigación (SCAI). University of Málaga. Spain..
Department of Chemistry. University of Crete. Greece.

Projects: PID2019-110249RB-I00, TED2021-129836B-I00, PID2023-148883OB-I00 & B1-2023_006 (UMA)
Predoctoral Grant: PRE2020-094459