

# ChemSusChem

## Supporting Information

### **Effect of the Electrolyte on the Oxygen Reduction Reaction with a MOF Embedded Co-Porphyrin**

Dana Rademaker, Stefania Tanase, and Dennis G. H. Hetterscheid\*

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## 2. Calculate turn-over frequency

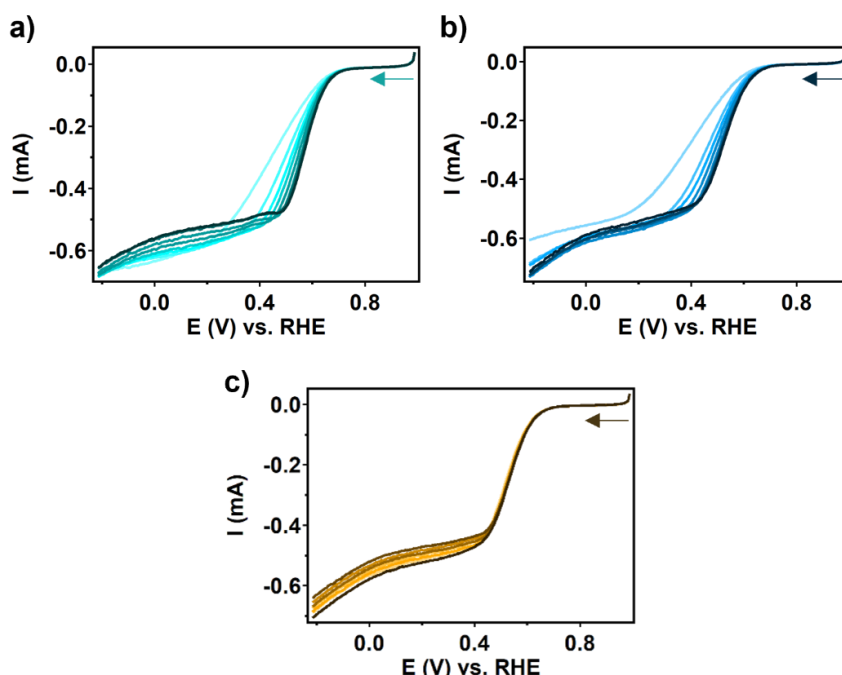
The turn-over frequency (TOF) was calculated for the two-electron reduction of oxygen to hydrogen peroxide. In Chapter 3 the selectivity of the ORR with PCN-224(Co) towards  $H_2O_2$  was confirmed. Therefore, the equation to derive the TOF is:<sup>[1]</sup>

$$TOF = \frac{\text{moles of } H_2O_2 \text{ formed}}{\text{moles of cobalt sites} \times \text{time}} = \frac{i_{cat}/(2F)}{N}$$

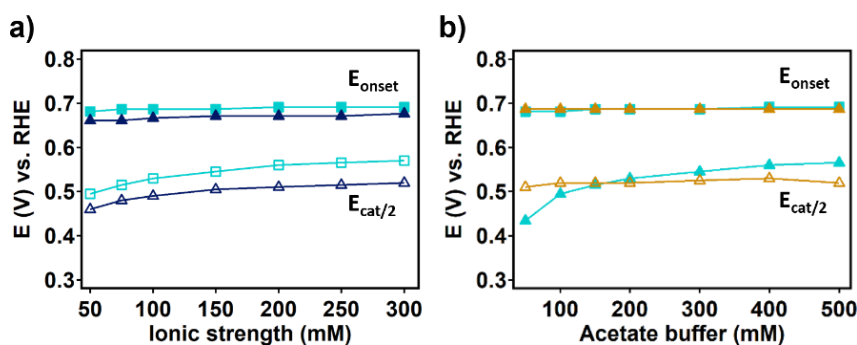
With  $i_{cat}$  as the catalytic current (A or C/s), F as Faradays constant ( $96485 \text{ C mol}^{-1}$ ), and N as total moles of cobalt sites.

The loading on the electrode is  $75 \mu\text{g}$  of PCN-224(Co), which equals  $0.055 \mu\text{mol}$  of cobalt sites. The TOF is determined as a function of all cobalt sites.

## 3. Buffer dependence study with CoTCPP

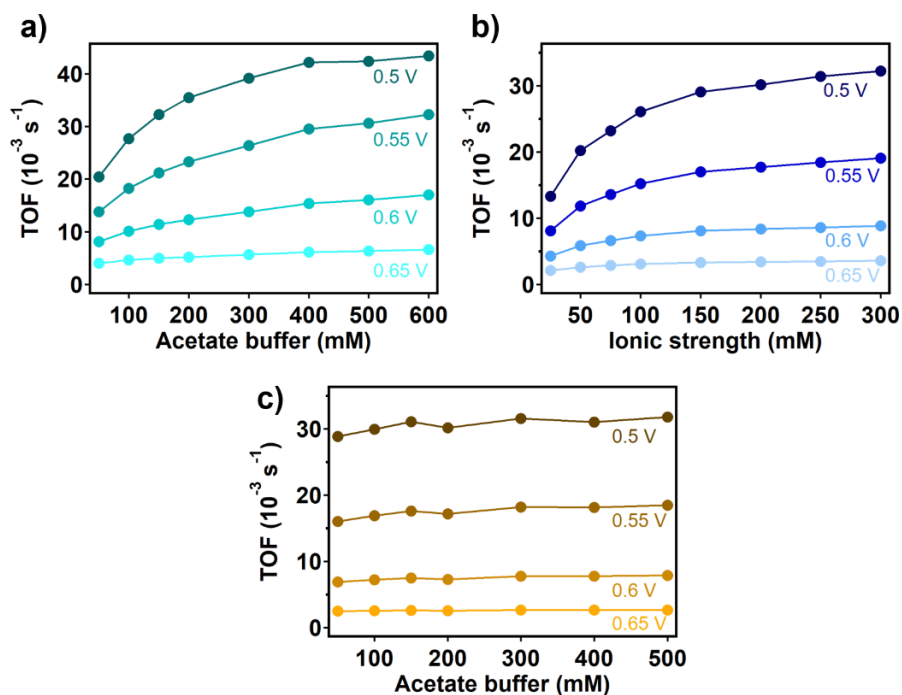


**Figure S1.** RDE LSV traces of CoTCPP in (a) sodium acetate buffer (pH 4.7) with concentrations of 50, 100, 150, 200, 300, 400, 500, and 600 mM (from light to dark); (b) sodium acetate buffer (pH 4.7, 50 mM) with increasing  $NaNO_3$  concentrations of 0, 25, 50, 75, 125, 175, 225, and 275 mM (from light to dark); and (c) in an electrolyte of  $NaNO_3$  and sodium acetate buffer at a constant ionic strength of 300 mM, while changing the sodium acetate buffer to 50, 100, 150, 200, 300, 400, and 500 mM (from light to dark). Measured with 50 mV/s scan rate and 1600 rpm rotation rate under an oxygen atmosphere.



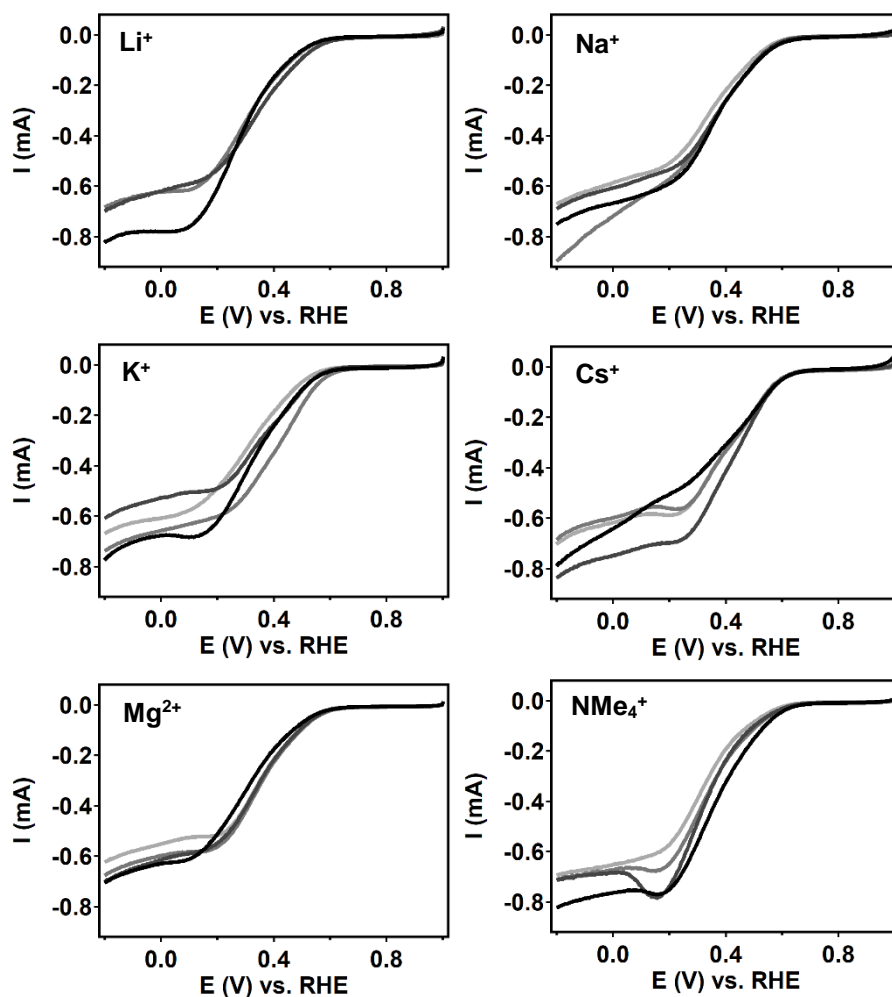
**Figure S2.** Analysis of RDE LSV traces of CoTCPP with (a)  $E_{onset}$  and  $E_{cat/2}$  as a function of the ionic strength of the sodium acetate dependence between 50 – 300 mM ionic strength of sodium acetate buffer (teal) and the ionic strength dependence with 50 mM of sodium acetate and  $NaNO_3$  as supporting electrolyte (dark blue). (b)  $E_{onset}$  and  $E_{cat/2}$  as a function of the sodium acetate buffer concentration

between 50 – 300 mM ionic strength of sodium acetate buffer (teal) and the sodium acetate buffer dependence with supporting  $\text{NaNO}_3$  electrolyte to achieve a fixed ionic strength of 300 mM (orange).



**Figure S3.** The TOF at 0.35, 0.4, 0.45, and 0.5 V vs. RHE (a) as a function of the sodium acetate buffer concentration between 50 – 300 mM ionic strength of sodium acetate buffer, (b) as a function of the ionic strength with a constant 50 mM of sodium acetate and variable  $\text{NaNO}_3$  concentration as supporting electrolyte, and (c) as a function of the sodium acetate buffer concentration of the sodium acetate buffer dependence with supporting  $\text{NaNO}_3$  electrolyte to achieve a fixed ionic strength of 300 mM.

### 3. LSV traces of PCN-224(Co) in various cation acetate buffers

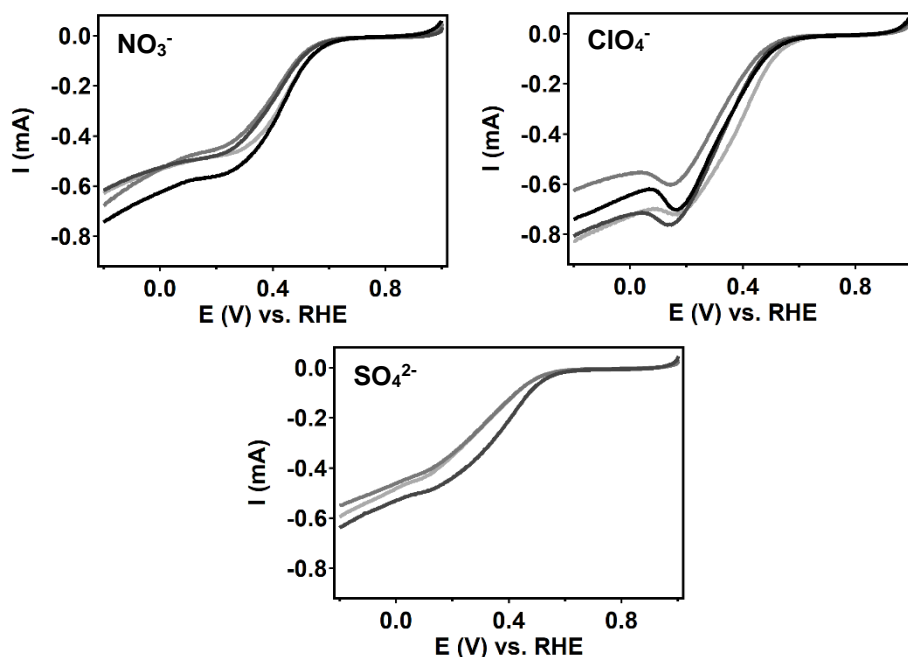


**Figure S4.** RDE LSV traces of PCN-224(Co) in 500 mM acetate buffer with lithium, sodium, potassium, cesium, magnesium, or tetramethylamine as cationic species. Measured with 50 mV/s scan rate and 1600 rpm rotation rate under an oxygen atmosphere.

**Table S1.** Turn-over frequencies of ORR with PCN-224(Co) in different cation acetate buffer solutions as a function of the applied potential.<sup>[2]</sup>

Metal Cation Properties			TOFs ( $10^{-3} \text{ s}^{-1}$ ) in case of [Cation]OAc.			
Ion	Ionic Radius (Å)	Hydrated Radius (Å)	0.5 V	0.45 V	0.4 V	0.35 V
Li <sup>+</sup>	0.94	3.82	$7.0 \pm 1.7$	$11.8 \pm 2.4$	$17.9 \pm 2.5$	$25.4 \pm 2.6$
Na <sup>+</sup>	1.17	3.58	$10.7 \pm 1.1$	$17.0 \pm 1.5$	$23.9 \pm 2.0$	$32.2 \pm 2.8$
K <sup>+</sup>	1.49	3.31	$10.3 \pm 3.7$	$17.1 \pm 5.4$	$24.2 \pm 6.5$	$31.5 \pm 7.1$
Cs <sup>+</sup>	1.86	3.29	$17.4 \pm 1.3$	$25.6 \pm 2.7$	$33.0 \pm 4.5$	$40.9 \pm 6.1$
Mg <sup>2+</sup>	0.72	4.28	$8.3 \pm 1.0$	$13.6 \pm 1.6$	$20.0 \pm 2.2$	$28.2 \pm 2.9$
NMe <sub>4</sub> <sup>+</sup>	2.85	3.47	$10.6 \pm 2.7$	$16.3 \pm 4.1$	$23.7 \pm 5.2$	$33.5 \pm 6.1$

#### 4. LSV traces of PCN-224(Co) in electrolytes with various anions

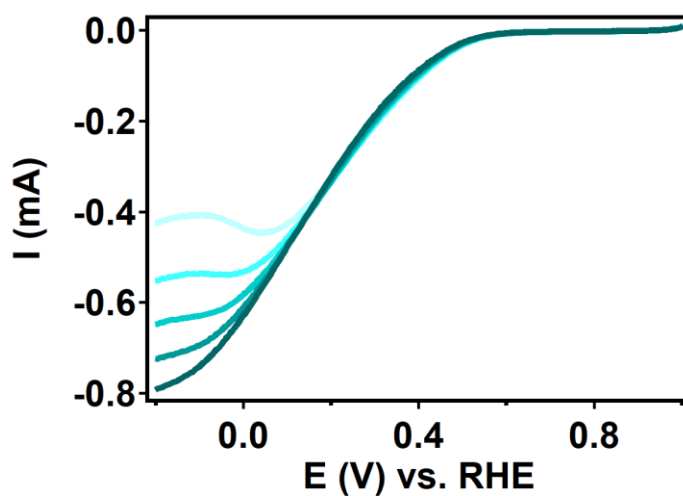


**Figure S5.** RDE LSV traces of PCN-224(Co) in 50 mM sodium acetate buffer with addition of sodium nitrate, sodium perchlorate, or sodium sulphate to obtain a 250 mM ionic strength solution. Measured with 50 mV/s scan rate and 1600 rpm rotation rate under an oxygen atmosphere.

**Table S2.** Turn-over frequencies of ORR with PCN-224(Co) in different sodium anion solutions as a function of the applied potential.<sup>[2]</sup>

Anion Properties			TOFs ( $10^{-3} \text{ s}^{-1}$ ) in case of Na[Anion].			
Ion	Ionic Radius (Å)	Hydrated Radius (Å)	0.5 V	0.45 V	0.4 V	0.35 V
CH <sub>3</sub> COO <sup>-</sup>	1.62	2.17	10.7 ± 1.1	17.0 ± 1.5	23.9 ± 2.0	32.2 ± 2.8
NO <sub>3</sub> <sup>-</sup>	1.79	2.23	10.7 ± 2.7	19.0 ± 4.2	28.2 ± 5.2	35.7 ± 5.3
ClO <sub>4</sub> <sup>-</sup>	2.50	2.69	7.1 ± 2.7	13.8 ± 4.7	23.1 ± 6.5	33.2 ± 7.1
SO <sub>4</sub> <sup>2-</sup>	2.30	2.73	4.8 ± 1.6	9.2 ± 3.0	14.9 ± 4.5	20.7 ± 5.4

## 5. Rotation rate dependence PCN-224(Co)



**Figure S6.** RDE LSVs at rotation rates between 400 and 2000 rpm with 400 rpm increments from light to dark colour with PCN-224(Co). Measured in 0.2 M acetate buffer (pH 4.7) with 50 mV/s scan rate under an oxygen atmosphere.

## 6. References

- [1] K. Dong, J. Liang, Y. C. Ren, Y. Y. Wang, Z. Q. Xu, L. C. Yue, T. S. Li, Q. Liu, Y. L. Luo, Y. Liu, S. Y. Gao, M. S. Hamdy, Q. Li, D. W. Ma, X. P. Sun, *J. Mater. Chem. A* **2021**, 9, 26019-26027.
- [2] a) A. G. Volkov, S. Paula, D. W. Deamer, *Bioelectrochem. Bioenerg.* **1997**, 42, 153-160; b) Y. Marcus, *J. Chem. Soc., Faraday trans.* **1991**, 87, 2995-2999.