Supporting Information

Amorphous Cobalt Vanadium Oxide as a Highly Active Electrocatalyst for Oxygen Evolution

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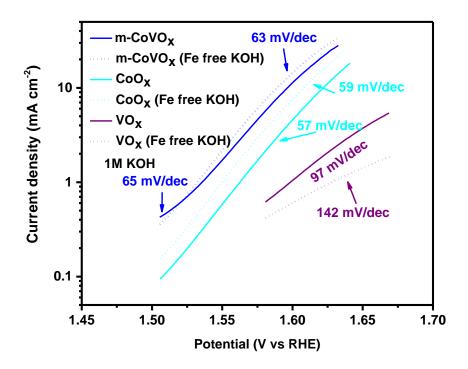


Figure S1. Tafel slopes of m- $CoVO_x$, CoO_x and VO_x in 1 M KOH and 1 M Fe-free KOH.

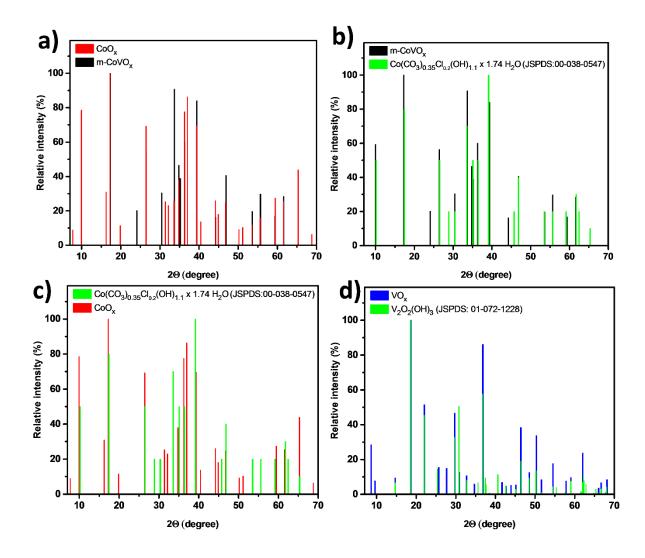


Figure S2. a) Comparison of extracted XRD peaks for m- $CoVO_x$ and CoO_x . b) Comparison of extracted XRD peaks for m- $CoVO_x$ and $Co(CO_3)_{0.35}Cl_{0.2}(OH)_{1.1} \cdot 1.74 H_2O$. c) Comparison of extracted XRD peaks for CoO_x and $Co(CO_3)_{0.35}Cl_{0.2}(OH)_{1.1} \cdot 1.74 H_2O$. d) Comparison of extracted XRD peaks for VO_x and $V_2O_2(OH)_3$.

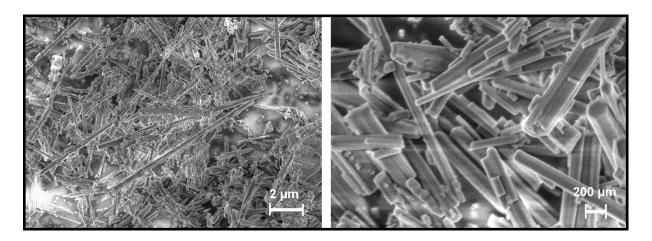


Figure S3. SEM images of CoO_x .

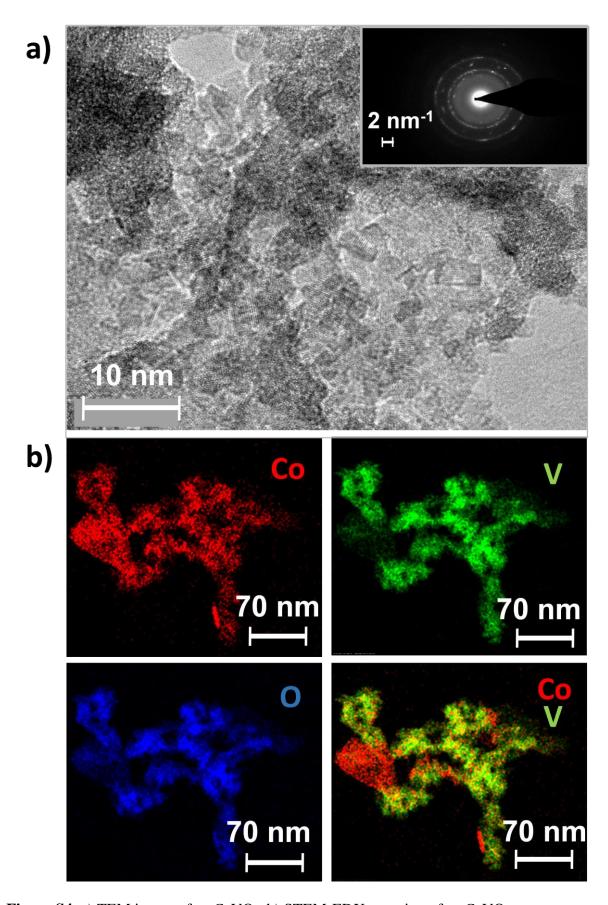


Figure S4. a) TEM image of m- $CoVO_x$. b) STEM-EDX mapping of m- $CoVO_x$.

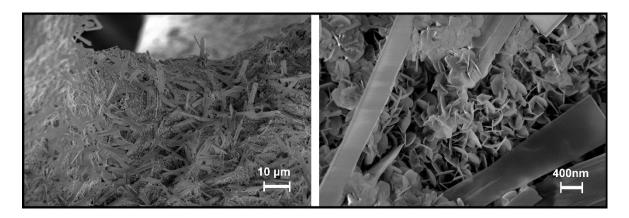


Figure S5. SEM images of m- $CoVO_x$ on nickel foam.

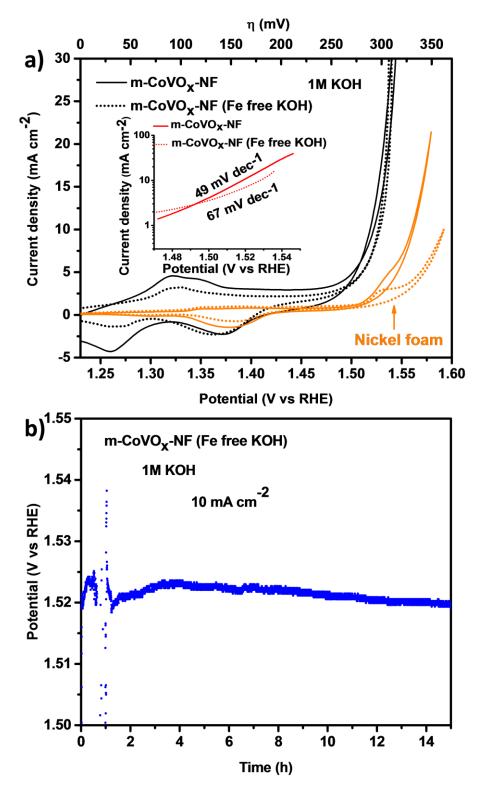


Figure S6. a) Polarization curves for $m\text{-}CoVO_x$ on nickel foam and extracted tafel slopes in 1 M KOH. Scan rate 1 mV s⁻¹; iR drop corrected. b) Stability of $m\text{-}CoVO_x$ on nickel foam at 10 mA cm⁻² in 1 M Fe-free KOH.

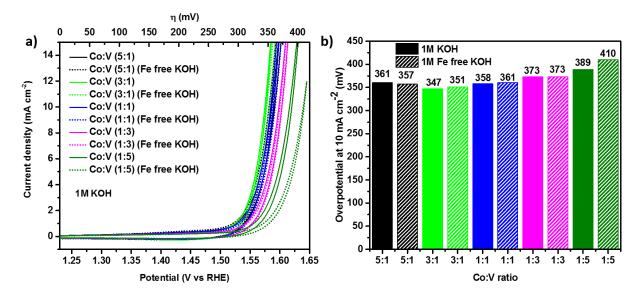


Figure S7. a) Polarization curves on glassy carbon of cobalt vanadium oxides synthesized with different Co:V ratio in the hydrothermal solution in 1 M KOH and 1 M Fe-free KOH. Scan rate 10 mV s⁻¹; iR drop corrected. b) Overpotentials for the different cobalt vanadium oxides with different Co:V ratios in 1 M KOH and 1 M Fe-free KOH at 10 mA cm⁻².

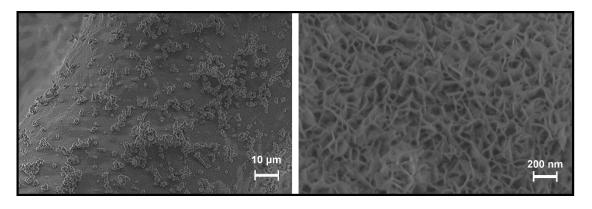


Figure S8. SEM images of a- $CoVO_x$ on nickel foam.

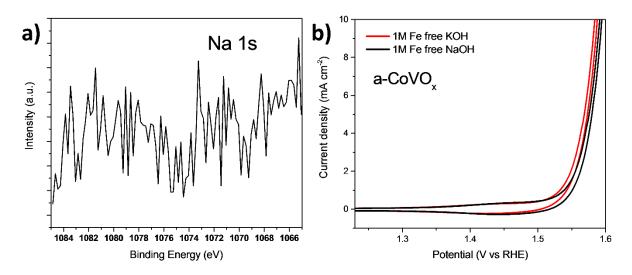


Figure S9. a) High resolution region spectra of Na 1s of XPS spectra of a- $CoVO_x$. b) Polarization curves on glassy carbon (loading 140 μ g cm⁻²) of a- $CoVO_x$ in 1 M Fe-free KOH and 1 M Fe-free NaOH. Scan rate 10 mV s⁻¹; iR drop corrected.

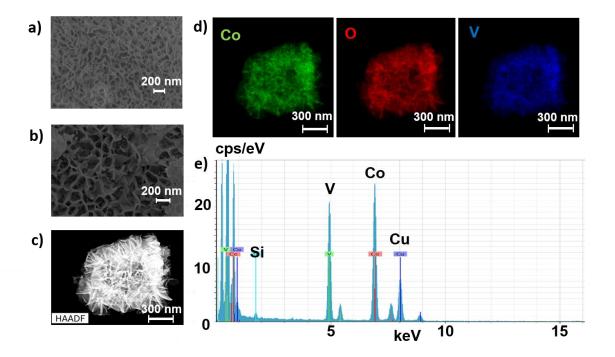


Figure S10. a) SEM image of $a\text{-}CoVO_x$ on nickel foam before electrolysis. b) SEM image of $a\text{-}CoVO_x$ on nickel foam after 15 h of electrolysis at 10 mA cm⁻² in 1 M Fe-free KOH. c) STEM image of $a\text{-}CoVO_x$ initially deposited on nickel foam. d) STEM-EDX mapping of $a\text{-}CoVO_x$ initially deposited on nickel foam after 15 h of electrolysis at 10 mA cm⁻² in 1 M Fe-free KOH. e) EDX spectrum of of $a\text{-}CoVO_x$ initially deposited on nickel foam after 15 h of electrolysis at 10 mA cm⁻² in 1 M Fe-free KOH.

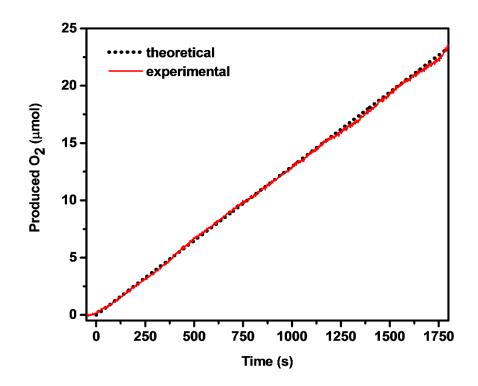


Figure S11. Agreement between measured and predicted moles of O_2 produced by a- $CoVO_x$ on nickel foam indicates nearly 100% faradaic efficiency. a-Co

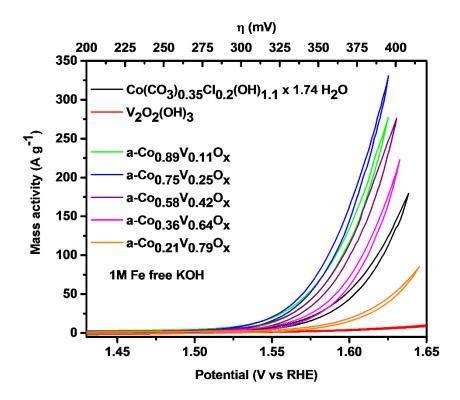


Figure S12. Mass activity of different a- $Co_yV_{1-y}O_x$ on glassy carbon (loading 140 μ g cm⁻²). Scan rate 10 mV s⁻¹; iR drop corrected.

Table S1. Comparison between the Co:V concentration ratios in the deposition solution and the Co:V ratios in the final catalysts determined by XPS.

| Catalyst | Deposition bath CoCl ₂ :VCl ₃ | XPS Co:V ratio (atomic %) |
|---|---|---------------------------|
| | ratio | |
| $Co_{0.89}V_{0.11}O_x$ | 5:1 | Co: 89%, V: 11% (9:1) |
| $\mathbf{Co}_{0.75}\mathbf{V}_{0.25}\mathbf{O}_{x}$ | 3:1 | Co: 75%, V: 25% (3:1) |
| $\mathbf{Co}_{0.58}\mathbf{V}_{0.42}\mathbf{O}_{x}$ | 1:1 | Co: 58%, V: 42% (3:2) |
| $Co_{0.36}V_{0.64}O_x$ | 1:3 | Co: 36%, V: 64% (2:3) |
| $\mathbf{Co}_{0,21}\mathbf{V}_{0,79}\mathbf{O}_x$ | 1:5 | Co: 21%, V: 79% (1:4) |
| | | |

Table S2. Bond strength of the different $Co_yV_{1-y}O_x$ for physical mixtures calculated using the method proposed by Bockris and Otagawa.¹

| Mixture of metal hydroxides | M-OH bond strength (kcal mol ⁻¹) |
|-----------------------------|--|
| Со-ОН | 130.4 |
| 0.89 Co-OH + 0.11 V-OH | 136.8 |
| 0.75 Co-OH + 0.25 V-OH | 144.9 |
| 0.58 Co-OH + 0.42 V-OH | 154.8 |
| 0.36Co-OH + 0.64 V-OH | 167.6 |
| 0.21 Co-OH + 0.79 V-OH | 176.3 |
| V-OH | 188.5 |

Table S3. Summary of the mass activities of the different oxides in 1 M KOH at $\eta = 350$ mV.

| Metal oxide | Mass activity (A g ⁻¹ at $\eta = 350$ mV) |
|---|--|
| $CoO_x (Co(CO_3)_{0.35}Cl_{0.2}(OH)_{1.1} \cdot 1.74 H_2O)$ | 19.2 |
| $Co_{0.89}V_{0.11}O_x$ | 56.3 |
| $Co_{0.75}V_{0.25}O_x$ | 69.5 |
| $Co_{0.58}V_{0.42}O_x$ | 45.6 |
| $Co_{0.36}V_{0.64}O_x$ | 25.4 |
| $Co_{0.21}V_{0.79}O_x$ | 6.8 |
| $VO_x (V_2O_2(OH)_3)$ | 2.1 |

Reference

(1) Bockris, J. O. M.; Otagawa, T. J. Electrochem. Soc. 1984, 131, 290-302.