

SUPPLEMENTARY MATERIAL

Manganese-Cobalt Geomimetic Materials for Supercapacitor Electrode

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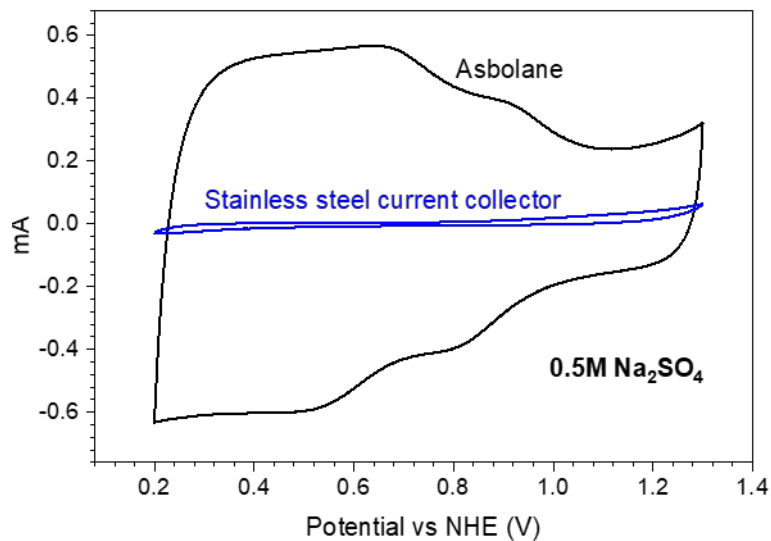


Figure S1 : Comparison of the CV curves of bare stainless-steel current collector with the one of Asbolane in 0.5M Na₂SO₄ at 5 mV/s. The capacity of bare current collector, which is directly proportional to the area of the voltammogram is negligible (lower than 2%) compared to this of asbolane material.

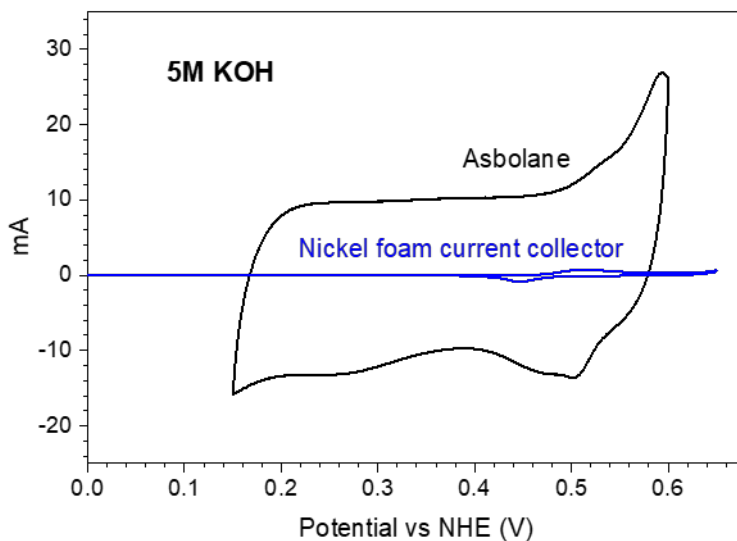


Figure S2 : Comparison of the CV curves of bare stainless-steel current collector with the one of Asbolane in 5M KOH at 10 mV/s. The capacity of bare current collector, which is directly proportional to the area of the voltammogram is negligible compared to this of asbolane material.

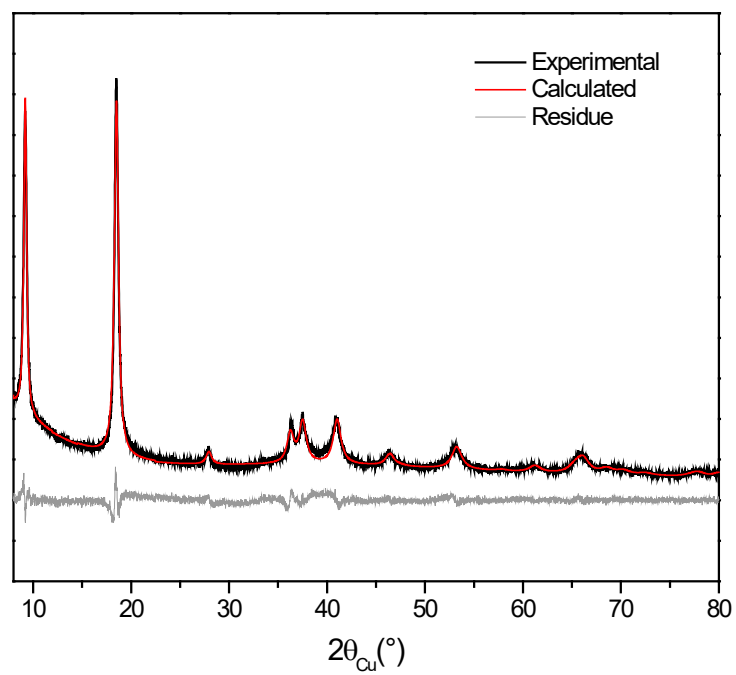


Figure S3 : Results of the Le Bail refinement for asbolane. The black curve corresponds to the experimental pattern and the red one to the calculated profile. The residue (grey curve) is also shown.

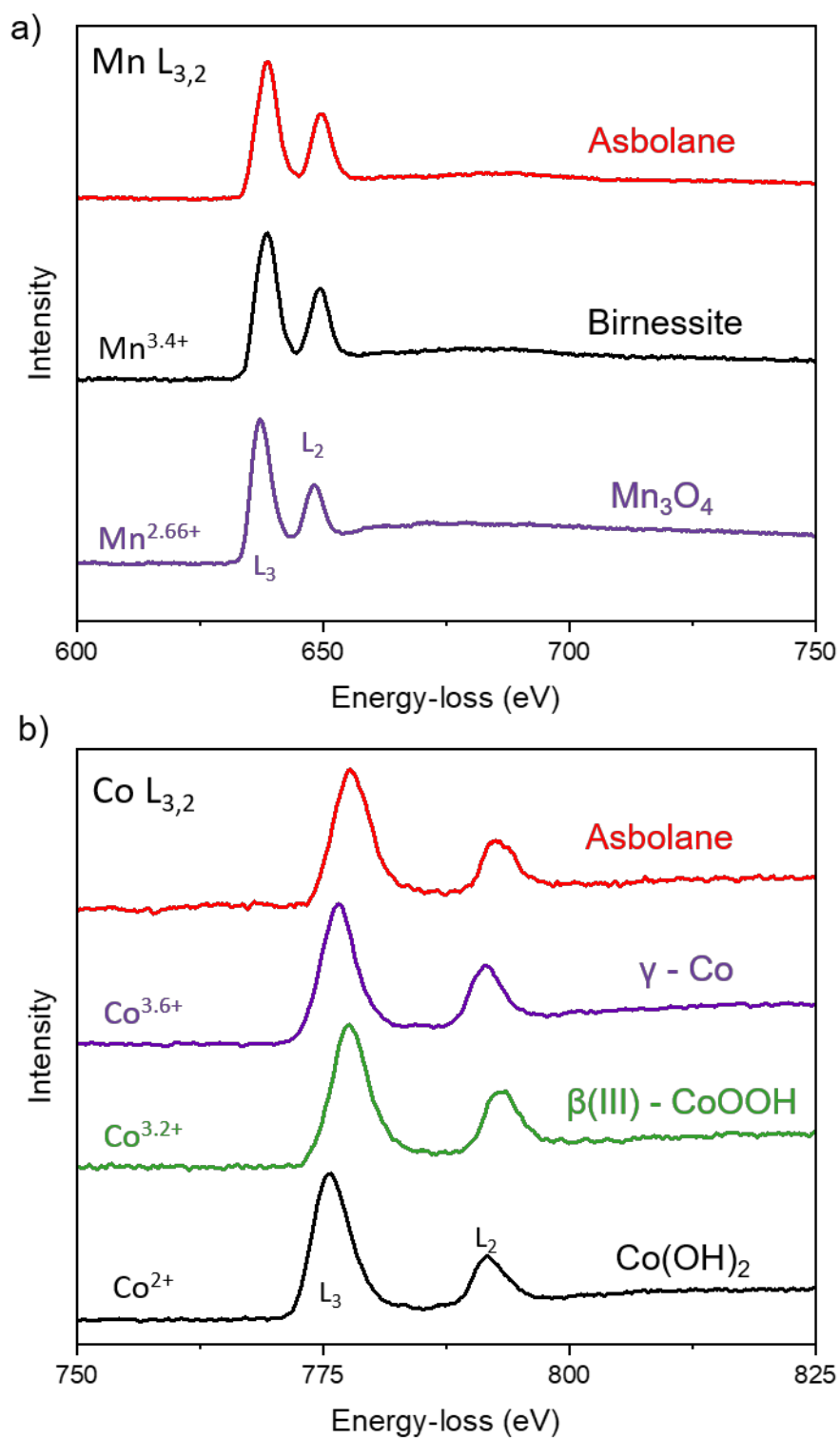


Figure S4 : Normalized EELS spectra for the references (Mn₃O₄, Birnessite, Co(OH)₂, β (III)-CoOOH, γ - Co) and Asbolane phases for a) Mn L_{3,2}, b) Co L_{3,2} edges and c) Table listing the oxidation degree of each materials and the calculated values of the intensity ratio L₃/L₂.

	Oxidation degree	L ₃ /L ₂ (Mn) Intensity	L ₃ /L ₂ (Co) Intensity
Mn₃O₄	Mn: +2.66	2.78	/
Birnessite	Mn: +3.4	2.26	/
Co(OH)₂	Co: +2	/	2.72
β(III) - CoOOH	Co: +3.2	/	2.31
γ- Co	Co: +3.6	/	2.24
Asbolane	Presence of Co ²⁺ , Co ³⁺ , Mn ³⁺ , Mn ⁴⁺	2.21	2.53

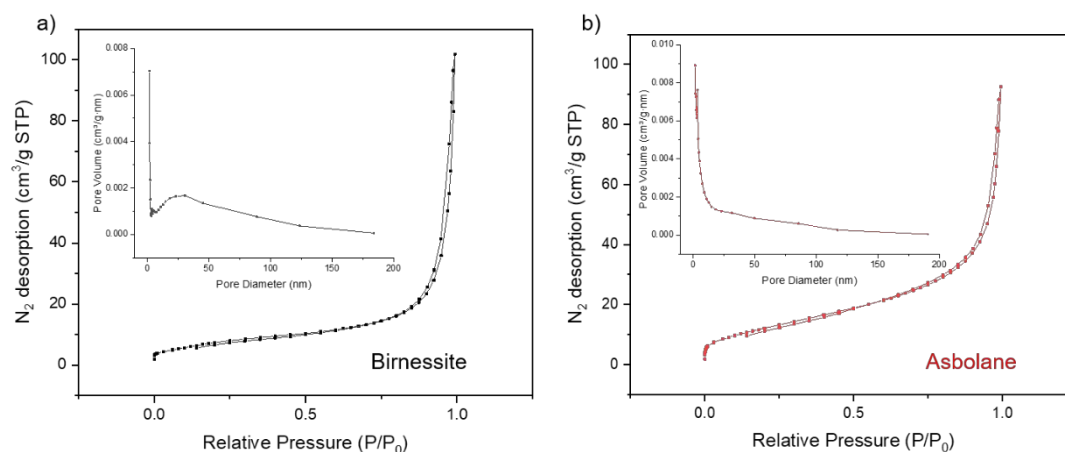


Figure S5 : N₂ adsorption/desorption isotherms obtained as well as the curves representing the pore size distribution as a function of their volume for a) Birnessite and b) Asbolane phases.

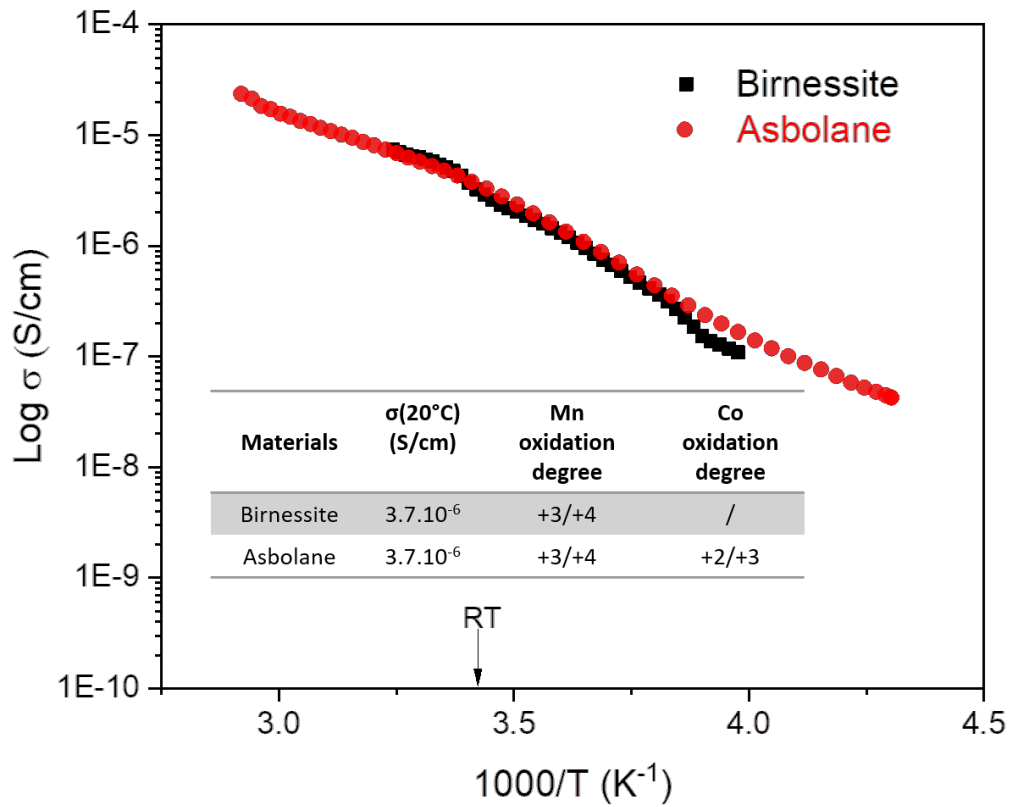


Figure S6 : Thermal variation of electronic conductivity and table summarizing the electronic conductivity values at 20°C as well as the oxidation degree of cobalt and manganese for Birnessite and Asbolane materials.

0.5M Na₂SO₄

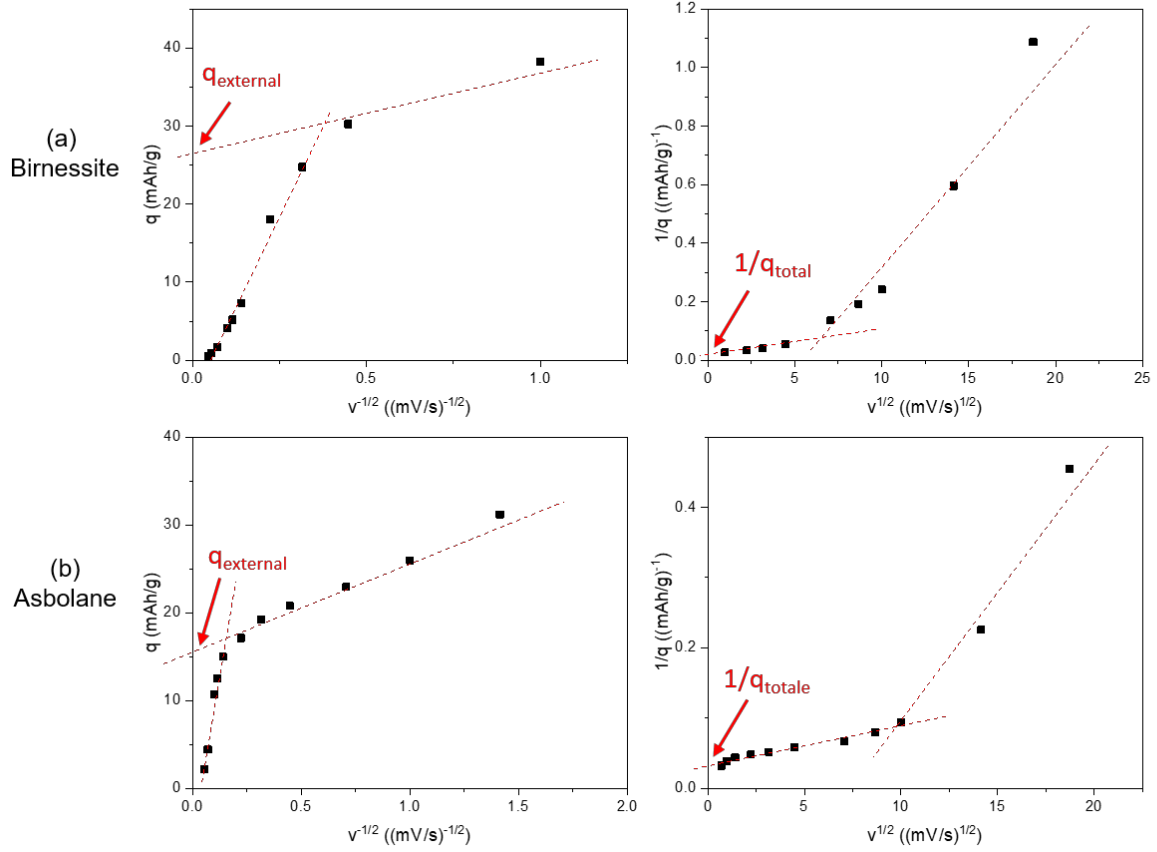


Figure S7 : Extrapolations at $v \rightarrow +\infty$ of $q = f(v^{-1/2})$ and at $v \rightarrow 0$ of $1/q = f(v^{1/2})$ for a) Birnessite and b) Asbolane materials for scan rates ranging from 0.5 to 350 mV/s in 0.5M Na₂SO₄.

5M KOH

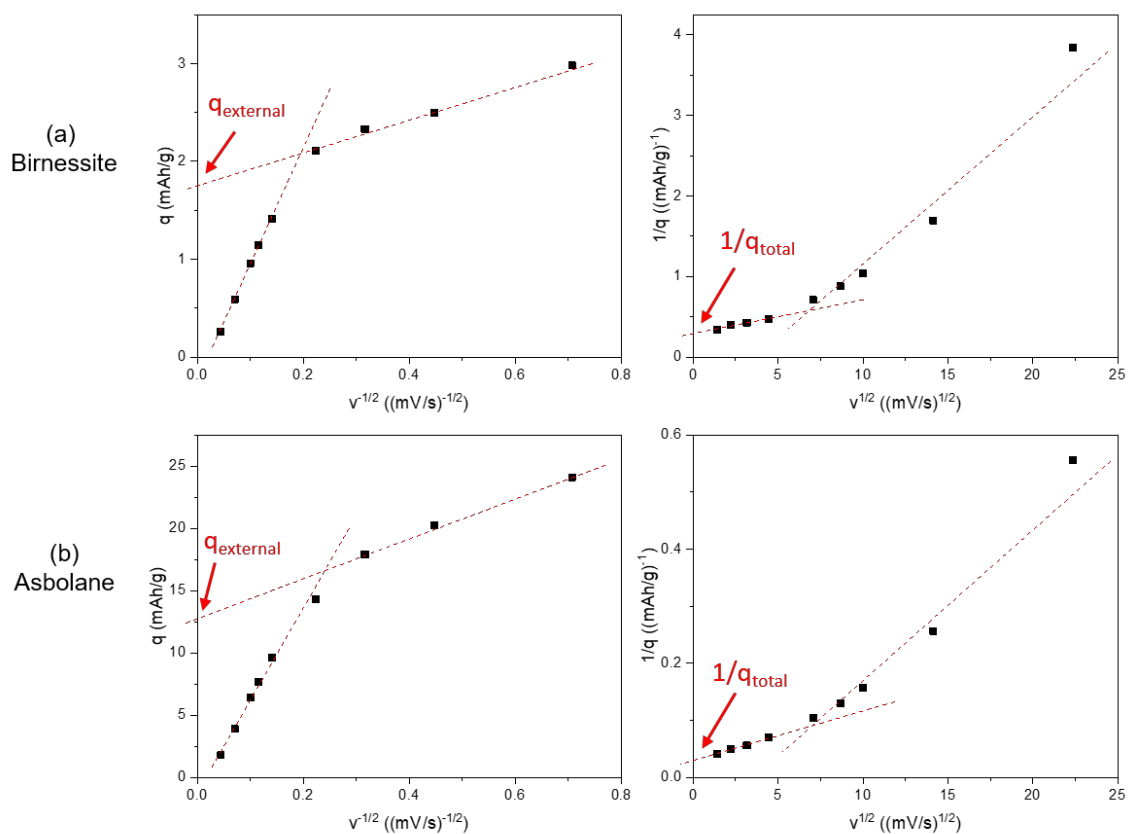


Figure S8 : Extrapolations at $v \rightarrow +\infty$ of $q = f(v^{-1/2})$ and at $v \rightarrow 0$ of $1/q = f(v^{1/2})$ for a) Birnessite and b) Asbolane materials for scan rates ranging from 2 to 500 mV/s in 5M KOH.

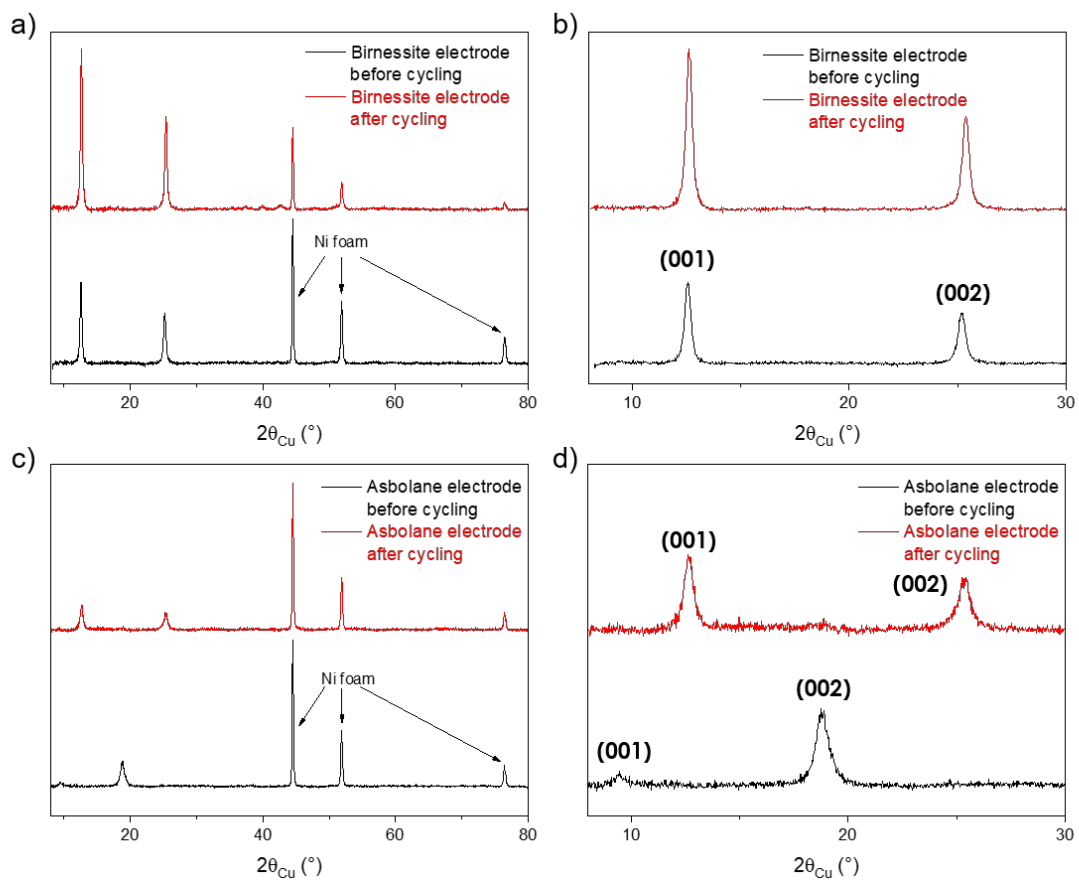


Figure S9 : X-ray diffractograms obtained before and after 3000 galvanostatic charge/discharge cycles at 1A/g in 5M KOH for a-b) Birnessite and c-d) Asbolane.

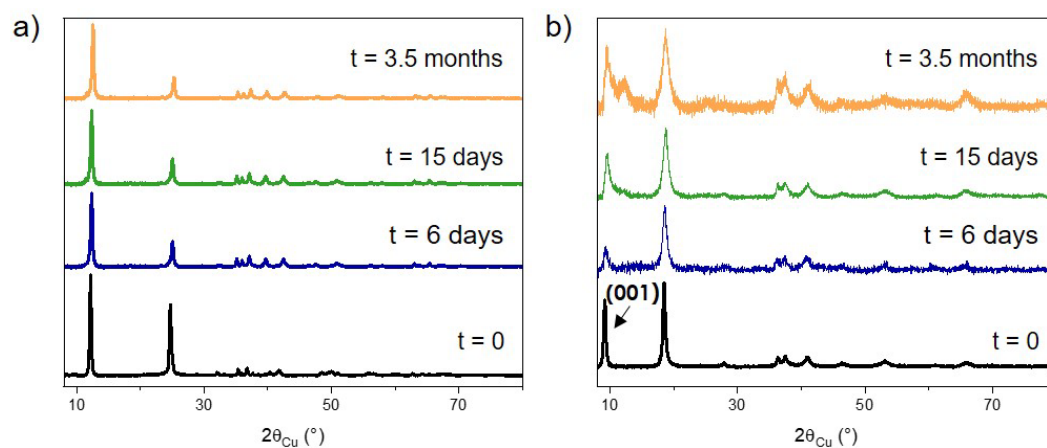


Figure S10 : X-ray diffractograms obtained before and after aging during 6 days, 15 days and 3.5 months in 5M KOH at room temperature for a) Birnessite and b) Asbolane materials.

Table S1 : Parameters used for simulating the X-ray diffraction profiles with the Diffax software.

	2 layers model	1 layer model
Wavelength	$\lambda_{\text{Cu}} = 1.5406 \text{ \AA}$	$\lambda_{\text{Cu}} = 1.5406 \text{ \AA}$
Point Group Symmetry	-3M	-3M
Unit Cell Parameters	$a = b = 2.84 \text{ \AA}$ $c = 9.6 \text{ \AA}$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	$a = b = 2.84 \text{ \AA}$ $c = 9.6 \text{ \AA}$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$
Instrumental Function	Pseudo-Voigt (Gaussian and Lorentzian contribution)	Pseudo-Voigt (Gaussian and Lorentzian contribution)
Atom Positions Notation used: Considered atom: x, y, z and occupancy	MnO ₂ layer = layer 1 O : 2/3 1/3 0.6 1 Mn : 0 0 0.5 1 O : 1/3 2/3 0.4 1 CoO ₂ layer = layer 2 O : 2/3 1/3 0.6 1 Co : 0 0 0.5 0.55 O : 1/3 2/3 0.4 1	Layer 1 : O : 0 0 0.7 1 Co : 1/3 2/3 0.6 0.55 O : 2/3 1/3 0.5 1 Mn : 0 0 0.4 1 O : 1/3 2/3 0.3 1
Translation Vectors Notation used: Transition probability, $\vec{x}, \vec{y}, \vec{z}$	Layer 1 to Layer 1 : 0 0 0 0 Layer 1 to Layer 2 : 1 0 0 z ₁ Layer 2 to Layer 1 : 1 0 0 z ₂ Layer 2 to Layer 2 : 0 0 0 0	Layer 1 to Layer 1 : 1 0 0 1

Table S2: Binding Energies (eV) and atomic percentages (at. %) extracted from XPS data for Birnessite and Asbolane.

Orbitals	Birnessite		Asbolane	
	B.E. (eV)	at. %	B.E. (eV)	at. %
C 1s	285.0	13.7	285.0	17.7
	286.5	2.6	286.7	2.2
	288.6	1.9	288.8	2.3
		18.2		22.2
O 1s	530.0	39.5	530.4	27.7
	531.6	7.7	531.6	20.6
	533.0	3.1	532.8	6.0
	534.6	2.8		
	53.2		54.3	
N 1s			398.7	0.1
			400.3	0.2
			403.6	0.1
			407.2	0.7
			1.8	
Ni 2p				
Mn 2p (Mn ⁺⁴)	642.6	9.3	642.7	10.7
Mn 2p (Mn ⁺³)	641.1	11.2	641.1	3.4
		20.5		14.1
Co 2p (Co ⁺³)			780.4	2.4
Co 2p (Co ⁺²)			781.0	6.0
				8.4
Na 1s		8.1		

Table S3 : q_{total} , q_{external} and q_{internal} values (in mAh/g and F/g) determined by Trasatti method in 5M KOH and 0.5M Na₂SO₄ for Birnessite and Asbolane.

	0.5M Na ₂ SO ₄			5M KOH		
	q_{total}	q_{external}	q_{internal}	q_{total}	q_{external}	q_{internal}
Birnessite	47.5 mAh/g (~156 F/g)	47.5 mAh/g (~156 F/g)	47.5 mAh/g (~156 F/g)	3.4 mAh/g (~27 F/g)	1.7 mAh/g (~13.5 F/g)	1.7 mAh/g (~13.5 F/g)
Asbolane	31.3 mAh/g (~102 F/g)	15.5 mAh/g (~51 F/g)	15.8 mAh/g (~51 F/g)	34.5 mAh/g (~276 F/g)	12.7 mAh/g (~27 F/g)	21.8 mAh/g (~13.5 F/g)