

Birnessite-clay mineral couple in the Rock Varnish: A nature's electrocatalyst

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Supplementary Information

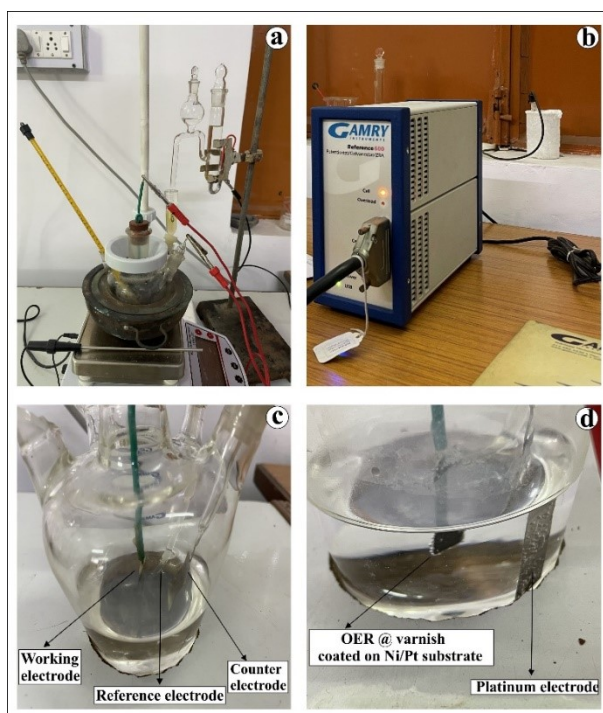


Fig.S1 (a, b) Electrochemical cell with Gamry's electrochemical station; (c) Conventional three electrode system; (d) RV/ Ni/Pt coated working electrode with Pt as counter electrode.

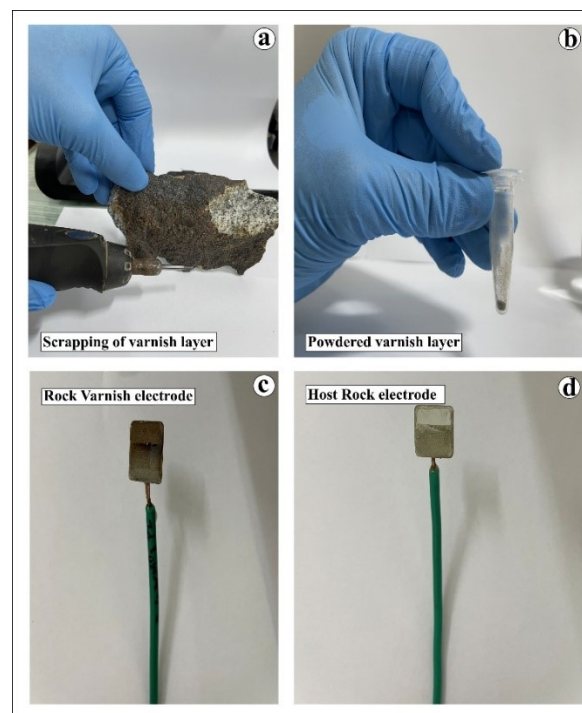


Fig.S2 (a) Scrapping of rock varnish layer for mineral electrode fabrication; (b) Powdered varnish layer; (c, d) Varnish, host rock working electrodes.

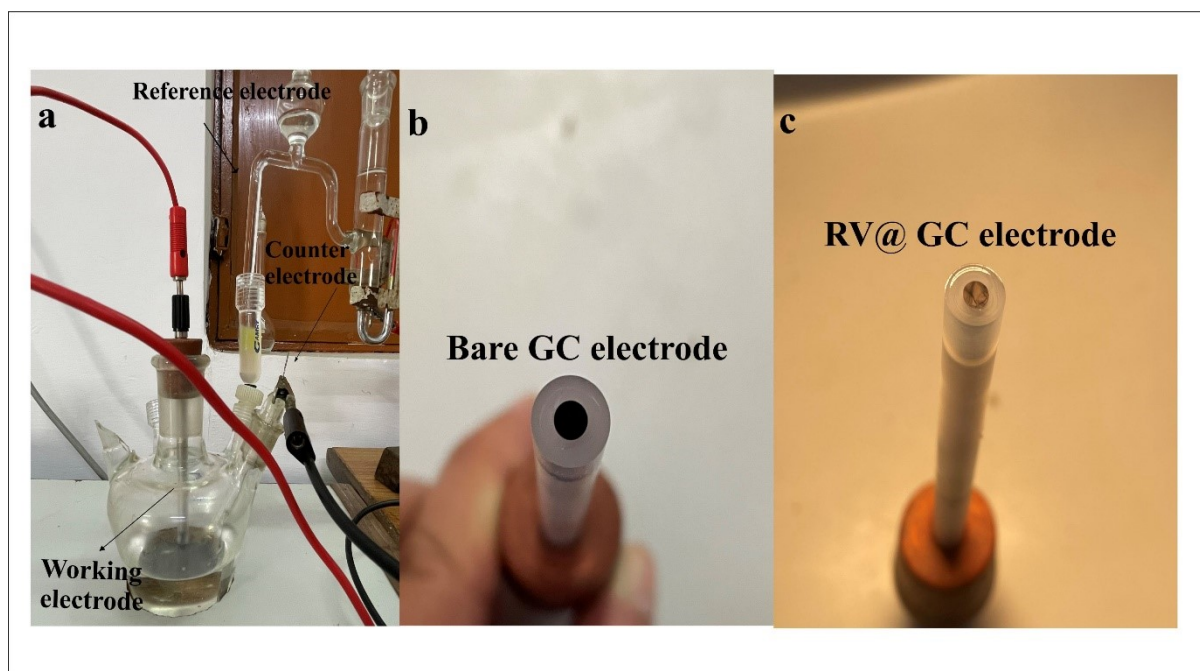


Fig.S3 (a) working setup for electrochemical measurements using (b) Bare Glassy carbon (GC) electrode and (c) Rock varnish (RV) coated on GC.

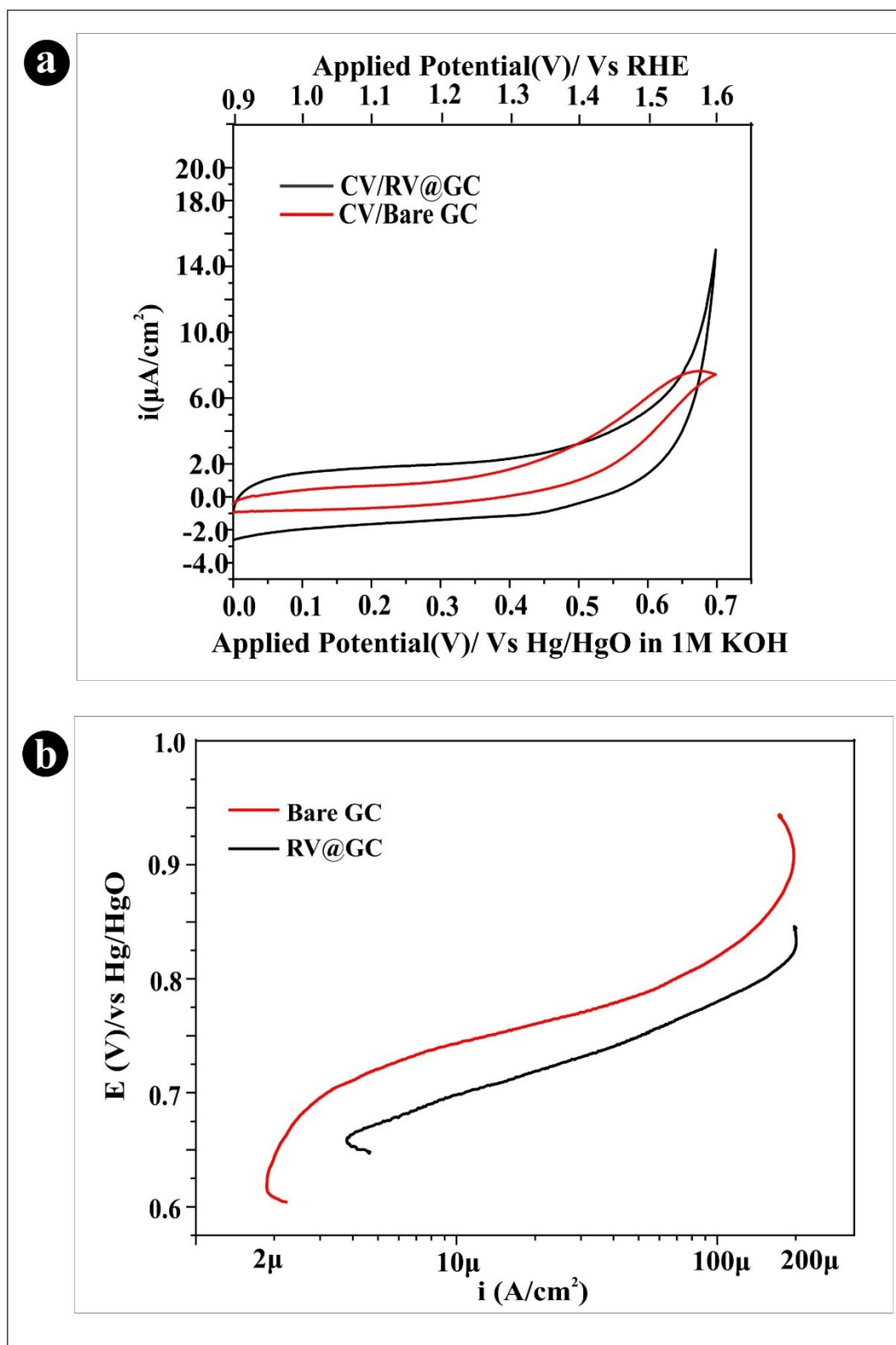


Fig.S4 (a) comparative Cyclic voltammograms of the rock varnish film coated on glassy carbon (GC) and bare Glassy carbon electrode at 20 mv/sec scan rate in 1M KOH at (25°C); **(b)** comparative Tafel plot for oxygen evolution on the bare GC electrode and RV coated on GC at 25°C in 1M KOH.

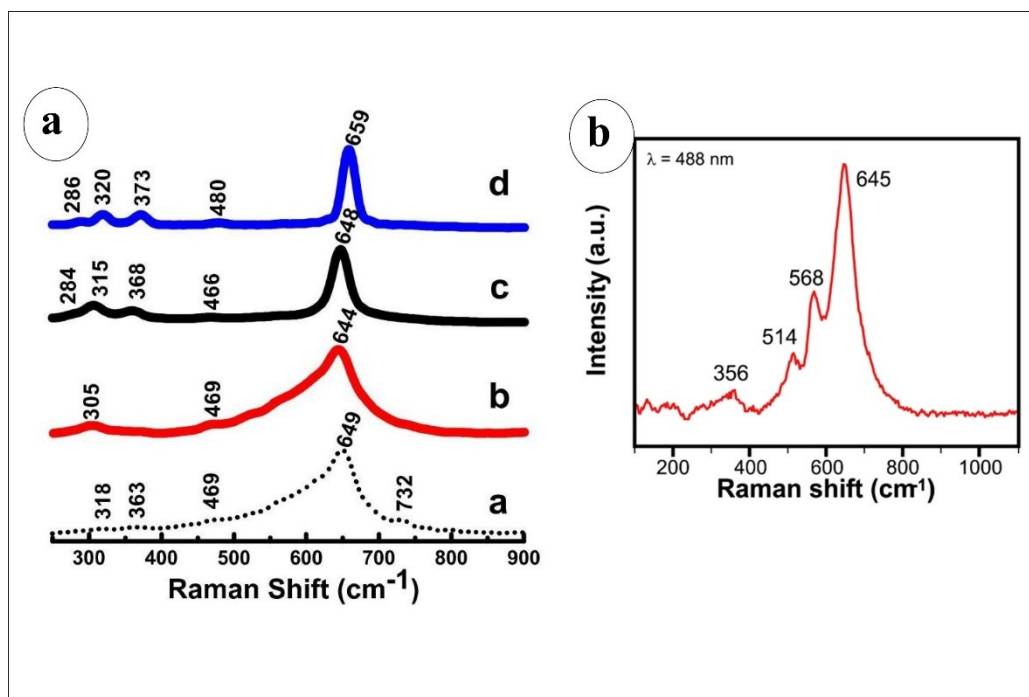


Fig. S5 (a) Raman spectra of MnO_x-373 K [a], MnO_x-573 K [b], α -Mn₂O₃ [c] and Mn₃O₄ [d] Reproduced with copyright permission from the journal “Evaluation of MnO_x, Mn₂O₃, and Mn₃O₄ Electrodeposited Films for the Oxygen Evolution Reaction of Water,” by Ramirez et al., 2014, *J. Phys. Chem. C*, 118, 26, 14073-14081, <https://pubs.acs.org/doi/10.1021/jp500939d> further permission related to the material excerpted should be directed to the ACS¹; (b) Raman spectrum of δ -MnO₂, Reproduced with copyright permission from the journal “Fast synthesis of δ -MnO₂ for a high-performance supercapacitor electrode²,” by Cremonuzzi et al., 2020, *SN Applied Sciences* 2:1689 | <https://doi.org/10.1007/s42452-020-03488-2>.

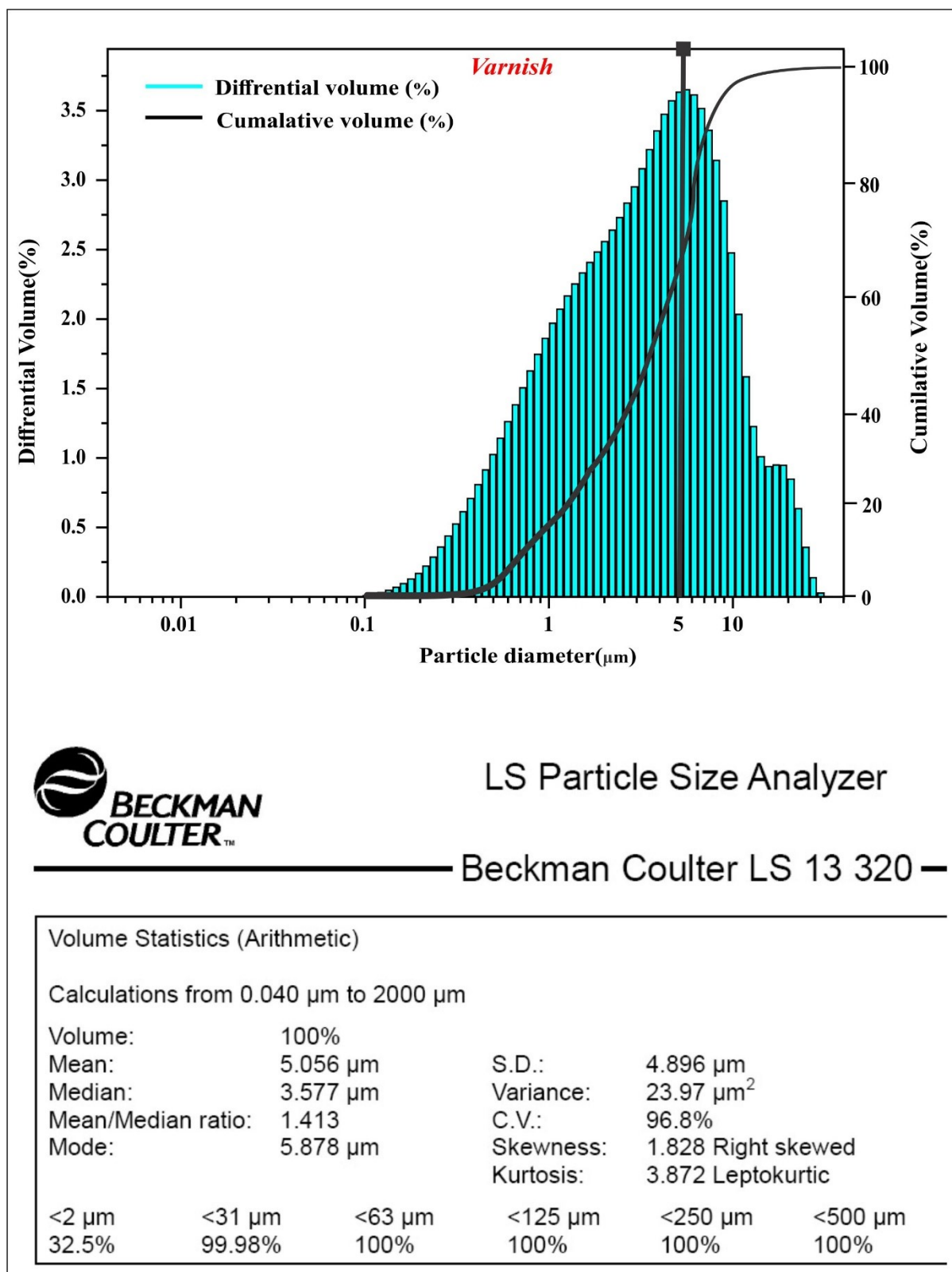


Fig. S6 Particle size distribution plot for the milled catalyst (varnish) depicting the average particle size in terms of differential and cumulative volume (%) confirming presence of clay sized particles in the varnish enhancing the adsorption-desorption process.

Table.S1 Cyclic Voltammetric parameters for the rock varnish film electrode on Ni at different scan rates in 1M KOH at 25°C.

Scan rate / mVsec ⁻¹	E _{Pa} /mV	E _{Pc} /mV	ΔE = E _{Pa} - E _{Pc} mV	E° = (E _{Pa} + E _{Pc}) /2 / mV	i _{Pa} / mA cm ⁻²	i _{Pc} / mA cm ⁻²	i _{Pa} / i _{Pc}
10	476	406.2	65.8	439.1	3.7	1.7	2.2
20	488.9	407.4	81.5	448.1	9.7	4.3	2.2
40	501.1	401.5	99.6	451.3	18.1	8.6	2.1
60	506.9	393.5	113.4	450.2	24.4	12.8	1.9
80	512.9	387.4	125.5	450.1	30.5	16.5	1.8
100	520.9	391.4	129.5	456.1	35.9	20.3	1.7

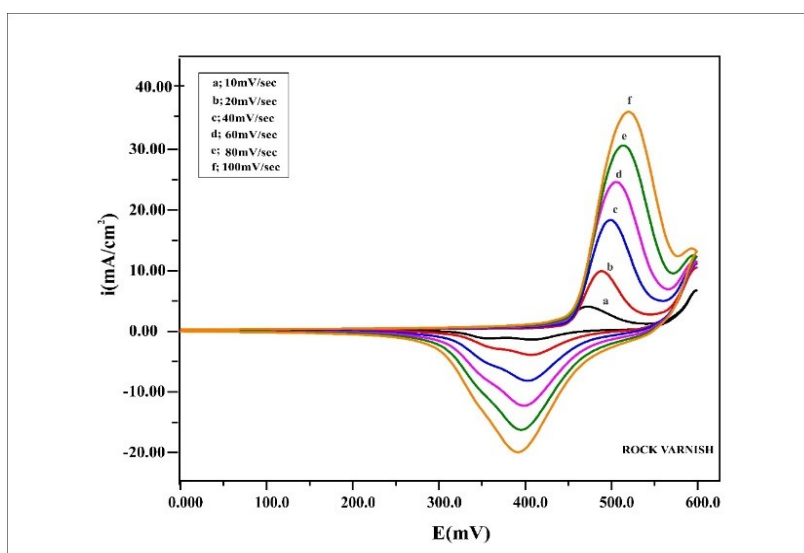


Fig. S7 Cyclic voltammograms of the Rock varnish film electrode on Ni at different scan rates in 1M KOH (25°C).

Table.S2 Cyclic Voltammetric parameters for the host rock film electrode on Ni at different scan rates in 1M KOH at 25°C.

Scan rate / mVsec ⁻¹	E _{Pa} / mV	E _{Pc} / mV	ΔE = E _{Pa} - E _{Pc} mV	E° = (E _{Pa} + E _{Pc}) / 2 / mV	i _{Pa} / mA cm ⁻²	i _{Pc} / mA cm ⁻²	i _{Pa} / i _{Pc}
10	473	357.5	115.5	415.2	5.9	3.7	1.6
20	487.9	354.5	133.4	421.2	8.8	5.7	1.5
40	516.8	349.6	167.2	433.2	12.7	8.8	1.4
60	539.9	340.7	199.2	440.3	15.2	11.1	1.4
80	539.9	340.7	199.2	440.3	17.9	13.2	1.4
100	547.9	337.4	210.5	442.6	20.6	14.8	1.4

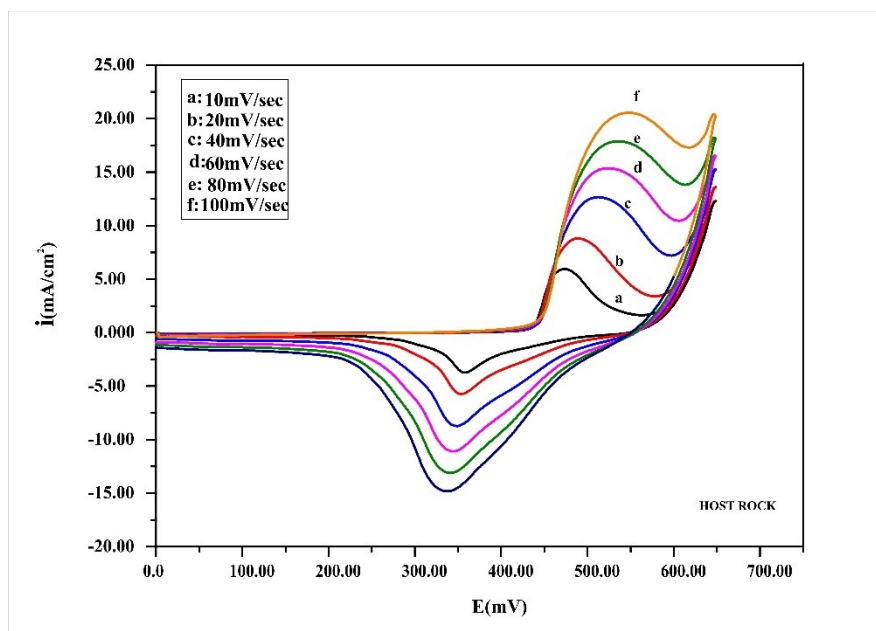


Fig. S8 Cyclic voltammograms of the host rock film electrode on Ni at different scan rates in 1M KOH (25°C).

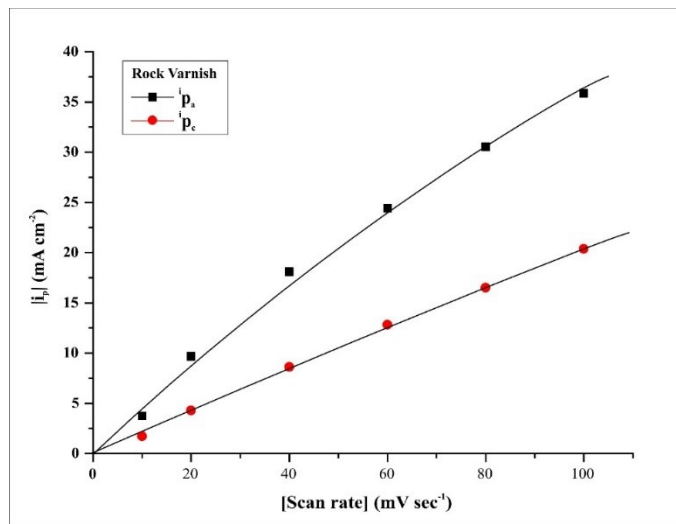


Fig. S9 The variation of anodic and cathodic peak currents as a function of scan rate for the Rock varnish film on Ni in 1M KOH (25°C).

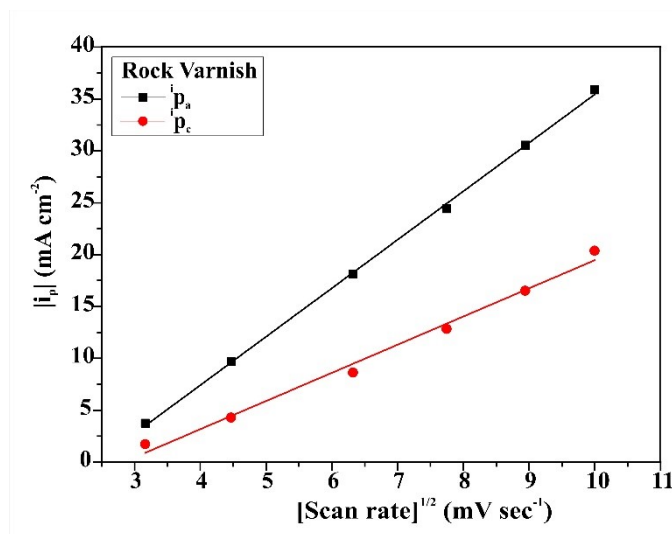


Fig. S10 Plot of $|i_p|$ vs (scan rate)^{1/2} for the Rock varnish film on Ni in 1M KOH (25°C).

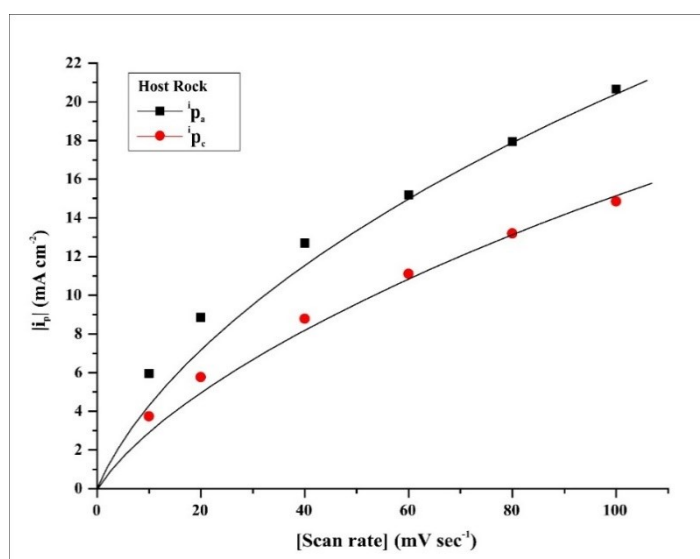


Fig. S11 The variation of anodic and cathodic peak currents as a function of scan rate for the host rock film on Ni in 1M KOH (25°C).

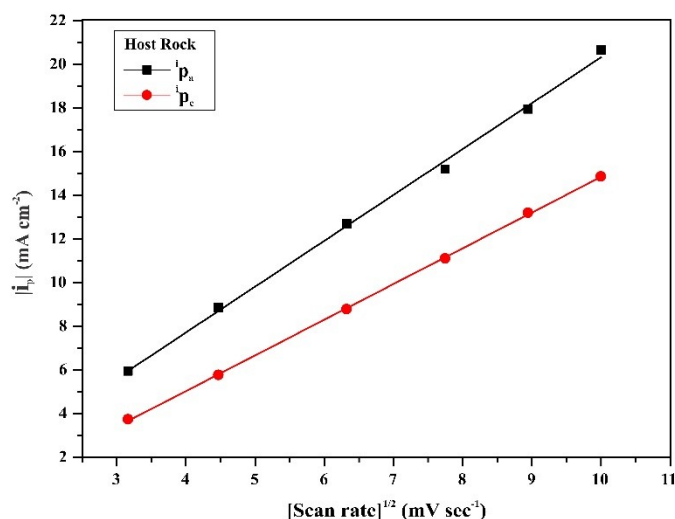


Fig. S12 Plot of $|i_p|$ vs $(\text{scan rate})^{1/2}$ for the Host rock film on Ni in 1M KOH (25°C).

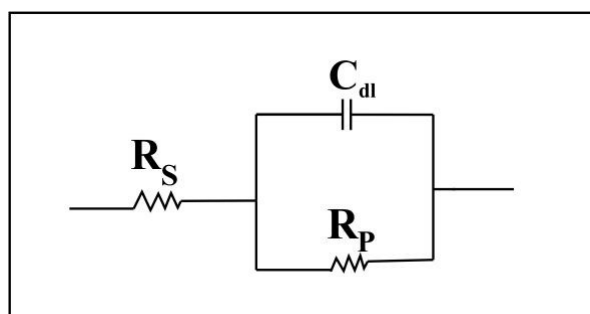


Fig.S13 Equivalent electronic circuit for a simple electrochemical cell

ESCA calculation method:

The ECSA of a catalyst sample is calculated from the CDL according to equation³ below:

$$\text{ECSA} = C_{DL}/C_s$$

where C_s is the specific capacitance of the sample or the capacitance of an atomically smooth planar surface of the material per unit area under identical electrolyte conditions. For our estimates of surface area, we use general specific capacitances $C_s = 0.040 \text{ mF/cm}^2$ in 1 M KOH based on typical reported values⁴.

Table S3: Concentration of major element oxide in varnish and host Rock

Element	Varnish Layer (%)	Host Rock (%)	Enrichment Factor (E.F.)
SiO ₂	61.02	69.84	1.20
Al ₂ O ₃	13.68	11.32	1.66
TiO ₂	0.66	0.91	1
Fe ₂ O ₃	8.83	8.85	1.37
MnO	1.98	0.08	34.1
MgO	1.54	5.25	0.40
CaO	3.07	4.85	0.87
Na ₂ O	1.87	3	0.85
K ₂ O	1.66	0.92	2.48
P ₂ O ₅	0.24	0.15	2.20

Enrichment factor was calculated by the equation⁵ as given below:

$$EF = A_e \cdot B_c / A_c \cdot B_e$$

A_e; Element concentration of sample to be determined

B_c; concentration of the reference element (in this case TiO₂)

A_c; element concentration of reference sample

B_e; Reference element concentration in sample to be determined

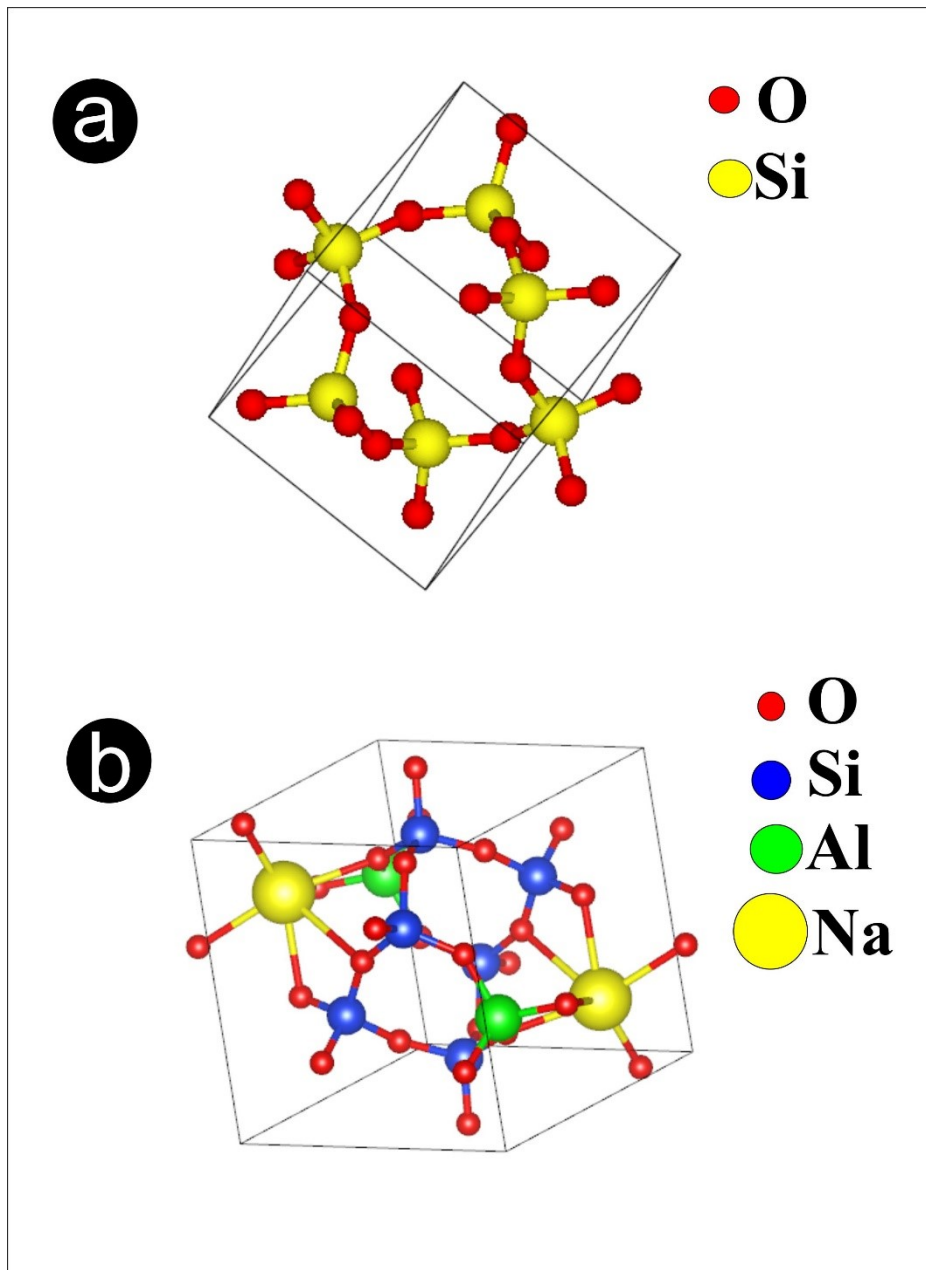


Fig.S14 (a, b) Polyhedral crystal structure of Quartz and albite present in varnish layer produced using the Vesta software.

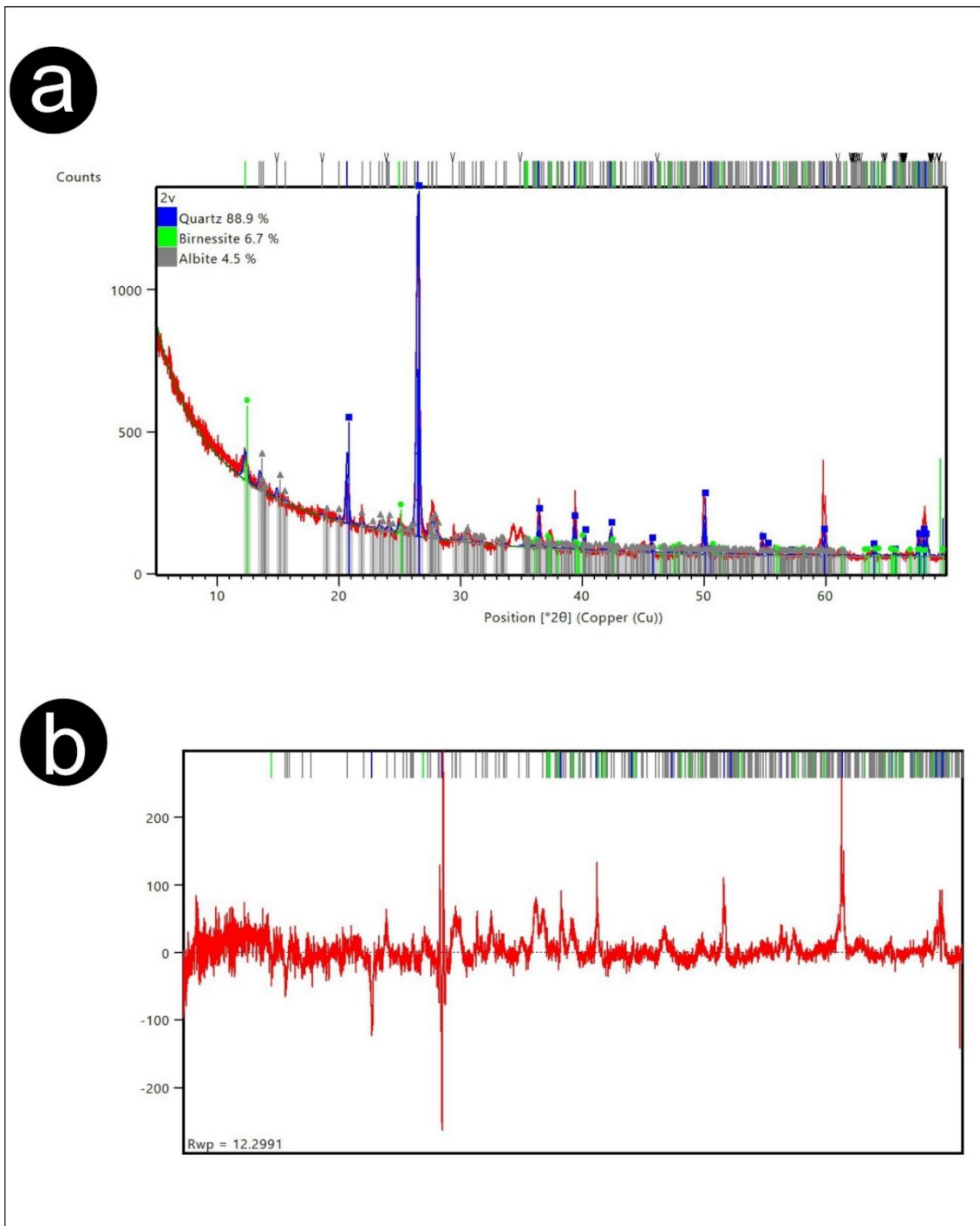


Fig.S15. (a) Rietveld refined Powder XRD pattern demonstrating the mineral phases contained in the rock varnish sample; (b) Difference plot between the measured and estimated Rietveld refined Powder XRD pattern.

Table S4. Structural data obtained after Rietveld refinement of Albite phase in varnish layer.

Lattice parameters	a (Å)	5.11914	Bond distances (Å)	Na - Na	7.99128
	b (Å)	7.45291		Al - Al	6.25135
	c (Å)	7.6952		Si - Si	3.81820
	α (°)	115.0514		Si - O	1.62512
	β (°)	107.0644		Na - O	2.36316
	γ (°)	100.6303		Al - O	1.73212
	Vol. (Å ³)	332.0394			
	Crystal system	Triclinic			
Point Group	-1				

Table S5. Structural data obtained after Rietveld refinement of quartz phase in varnish layer.

	a (Å)	4.91110		
	b (Å)	4.91110		
	c (Å)	5.39706		
	α (°)	90		
	β (°)	90		
	γ (°)	120		
Lattice parameters	Vol. (Å ³)	112.7315	Bond distances (Å)	Si – Si 3.05493
	Crystal system	Trigonal		Si – O 1.60877
	Point Group	321		

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