

Supporting Information

Robust and Bifunctional Electrodeposited NiCoCr Ternary Alloy for Alkaline Water Electrolysis

Jeffrey Tourneur, Corinne Lagrost and Bruno Fabre*

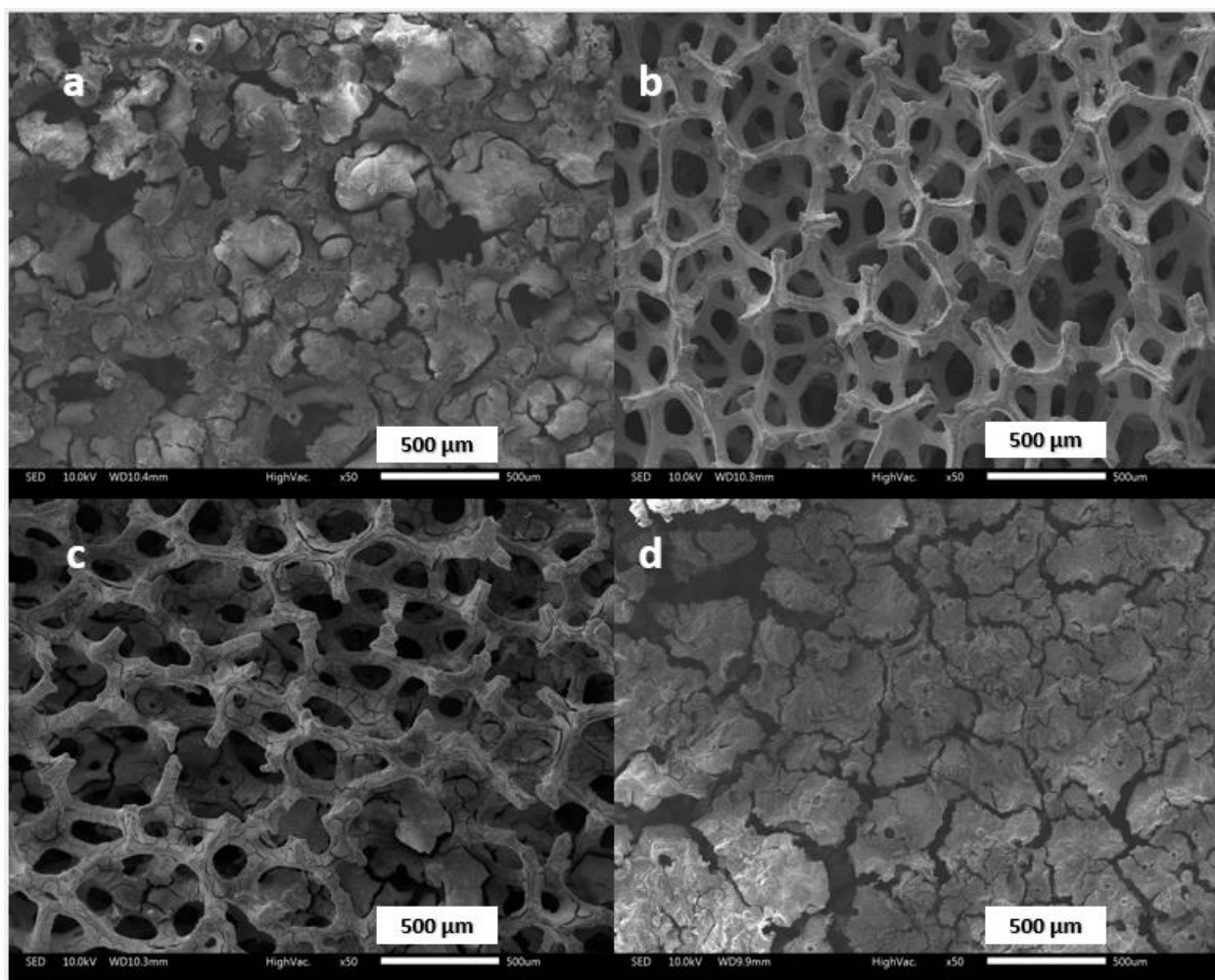


Figure S1. SEM images of NiCoCr electrodeposited on NF. Electrodeposition at -150 mA cm^{-2} (a, b), -75 mA cm^{-2} (c) and -225 mA cm^{-2} (d) for 10 min in an electrolytic bath containing 50 mM NiCl_2 , 12 mM CoCl_2 , 28 mM CrCl_3 , 30 mM ethylenediamine dihydrochloride and 50 mM boric acid (a, c, d), for 1 min in an electrolytic bath containing 100 mM NiCl_2 , 24 mM CoCl_2 , 56 mM CrCl_3 , 60 mM ethylenediamine dihydrochloride and 100 mM boric acid (b).

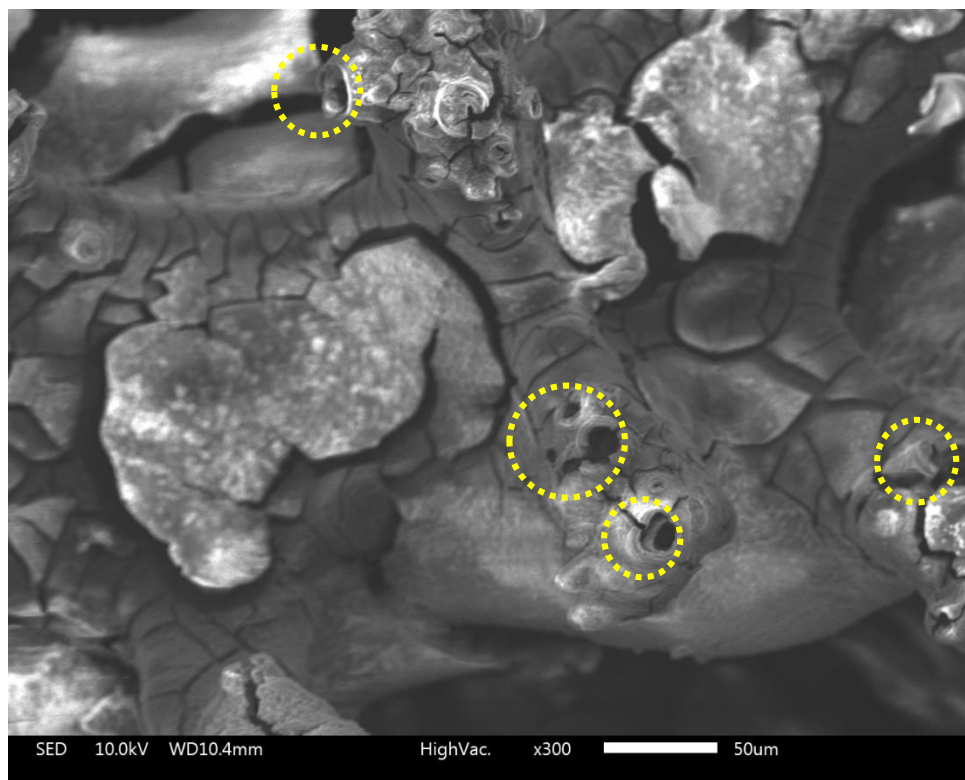
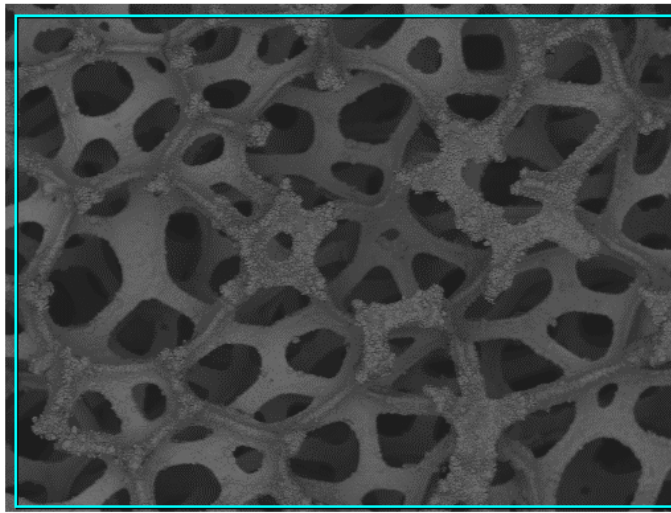


Figure S2. SEM image of a NiCoCr electrodeposited on NF at -150 mA cm^{-2} for 10 minutes in an electrolytic bath containing 50 mM NiCl₂, 12 mM CoCl₂, 28 mM CrCl₃, 30 mM ethylenediamine dihydrochloride and 50 mM boric acid. The release of H₂ bubbles during electrodeposition leads to the formation of crater-shaped structures in NiCoCr (highlighted by the dashed yellow circles).

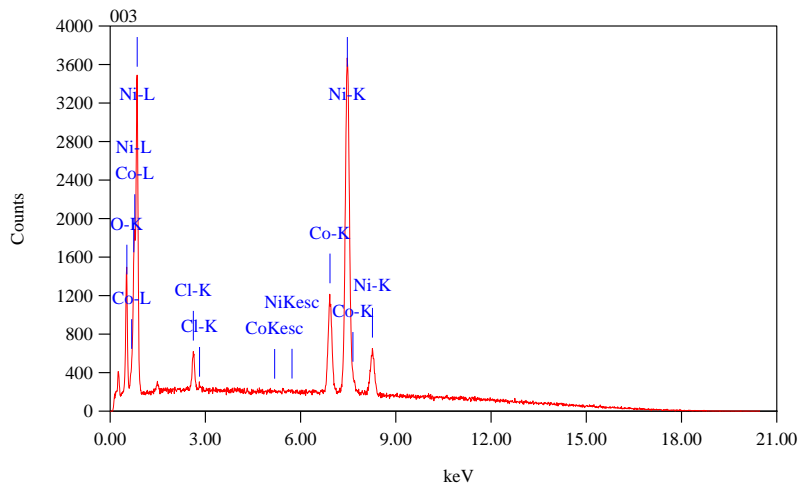
Image000

1/1



Title : IMG1

 Instrument : IT300 (LA)
 Volt : 20.00 kV



Acquisition Parameter
 Instrument : IT300 (LA)
 Acc. Voltage : 20.0 kV
 Probe Current: 7.47500 nA
 PHA mode : T3
 Real Time : 30.00 sec
 Live Time : 27.08 sec

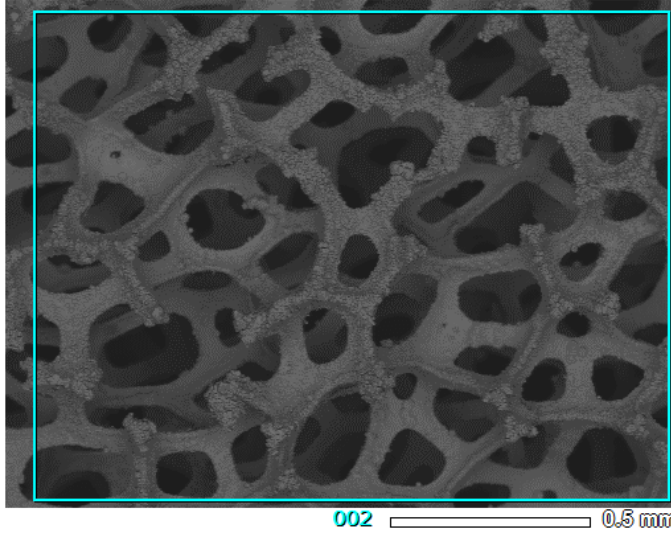
ZAF Method Standardless Quantitative Analysis

Fitting Coefficient : 0.0395

Element	(keV)	Mass%	Sigma	Atom%	Compound	Mass%	Cation	K
Cl K	2.621	1.67	0.04	2.28				1.5256
Co K	6.924	17.05	0.17	13.98				16.3685
Ni K	7.471	73.61	0.35	60.58				73.4408
O K	0.525	7.67	0.08	23.16				8.6651
Total		100.00		100.00				

Image001

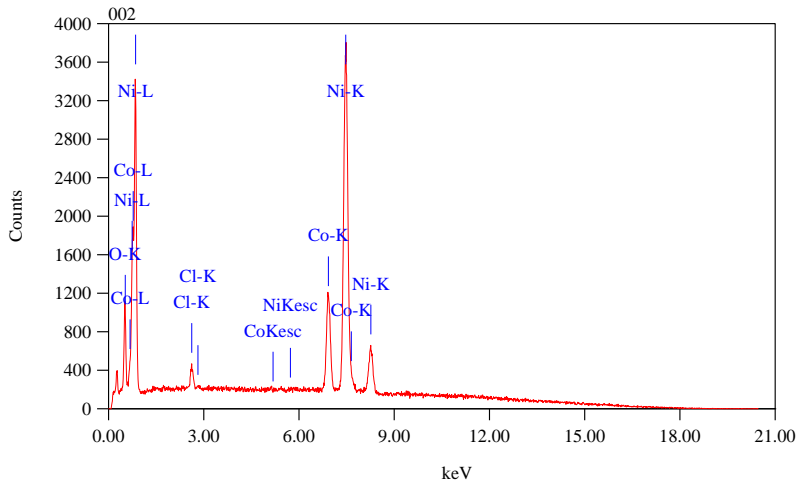
1/1



Title : IMG1

Instrument : IT300(LA)

Volt : 20.00 kV



Acquisition Parameter

Instrument : IT300(LA)

Acc. Voltage : 20.0 kV

Probe Current: 7.47500 nA

PHA mode : T3

Real Time : 30.00 sec

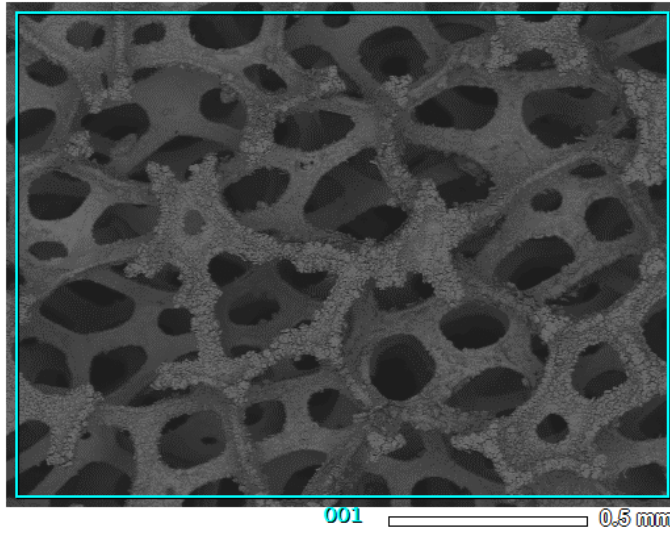
Live Time : 27.05 sec

ZAF Method Standardless Quantitative Analysis

Fitting Coefficient : 0.0340

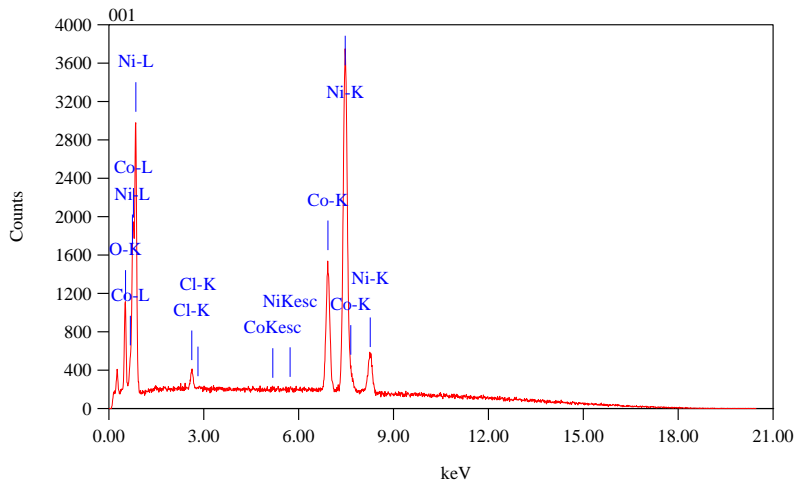
Element	(keV)	Mass%	Sigma	Atom%	Compound	Mass%	Cation	K
Cl K	2.621	0.98	0.03	1.40				0.8875
Co K	6.924	17.92	0.17	15.50				17.2408
Ni K	7.471	75.62	0.36	65.64				75.6238
O K	0.525	5.48	0.07	17.46				6.2479
Total		100.00		100.00				

Image002



Title : IMG1

Instrument : IT300(LA)



Acquisition Parameter

Instrument : IT300(LA)

Acc. Voltage : 20.0 kV

Probe Current: 7.47500 nA

PHA mode : T3

Real Time : 30.00 sec

ZAF Method Standardless Quantitative Analysis

Fitting Coefficient : 0.0378

Element	(keV)	Mass%	Sigma	Atom%	Compound	Mass%	Cation	K
Cl K	2.621	0.77	0.03	1.12				0.7060
Co K	6.924	21.97	0.18	19.04				21.1551
Ni K	7.471	71.82	0.34	62.49				71.8895
O K	0.525	5.43	0.07	17.35				6.2495
Total		100.00		100.00				

Figure S3. EDS spectra of NiCo electrodeposited on NF.

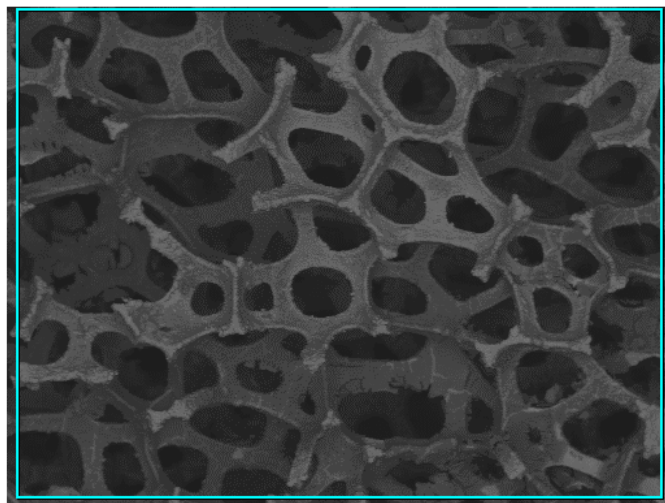
Image000

1/1

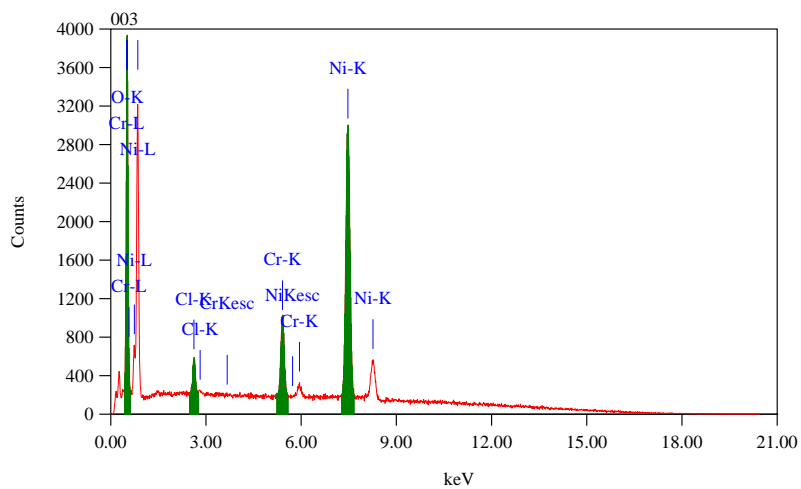
Title : IMG1

Instrument : IT300 (LA)

Volt : 20.00 kV



003 0.5 mm



Acquisition Parameter

Instrument : IT300 (LA)

Acc. Voltage : 20.0 kV

Probe Current: 7.47500 nA

PHA mode : T3

Real Time : 30.00 sec

Live Time : 27.28 sec

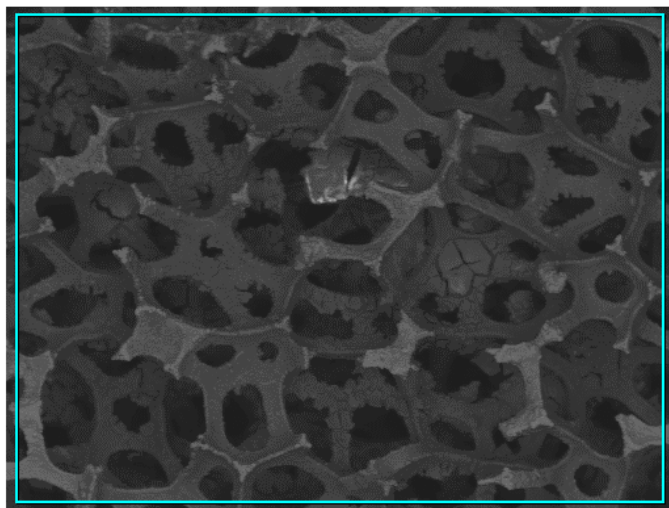
ZAF Method Standardless Quantitative Analysis

Fitting Coefficient : 0.0541

Element	(keV)	Mass%	Sigma	Atom%	Compound	Mass%	Cation	K
Cl K	2.621	1.76	0.04	1.78				1.5988
Cr K	5.411	8.42	0.10	5.80				8.5140
Ni K	7.471	66.74	0.35	40.73				63.0443

Image001

1/1

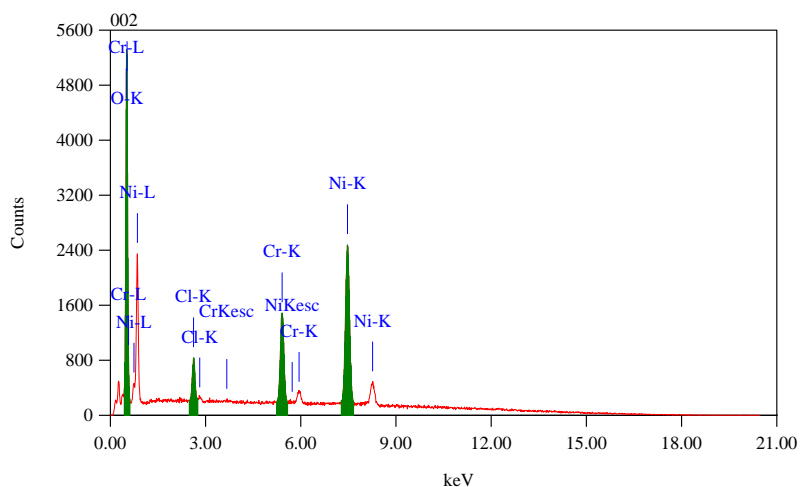


002 0.5 mm

Title : IMG1

Instrument : IT300 (LA)

Volt : 20.00 kV



Acquisition Parameter

Instrument : IT300 (LA)

Acc. Voltage : 20.0 kV

Probe Current: 7.47500 nA

PHA mode : T3

Real Time : 30.00 sec

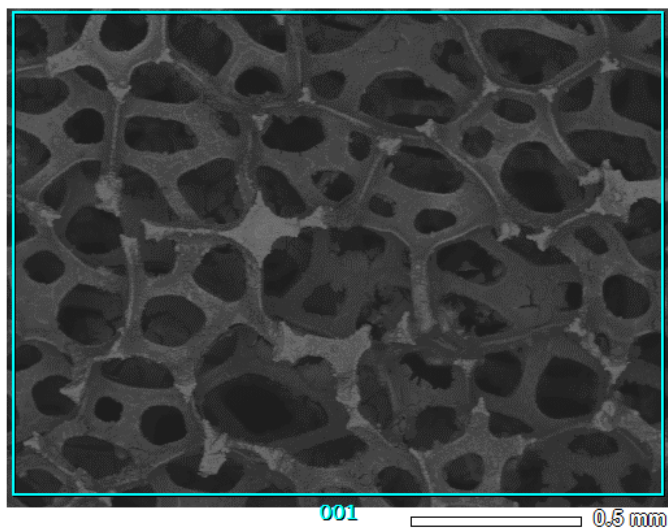
Live Time : 27.46 sec

ZAF Method Standardless Quantitative Analysis

Fitting Coefficient : 0.0705

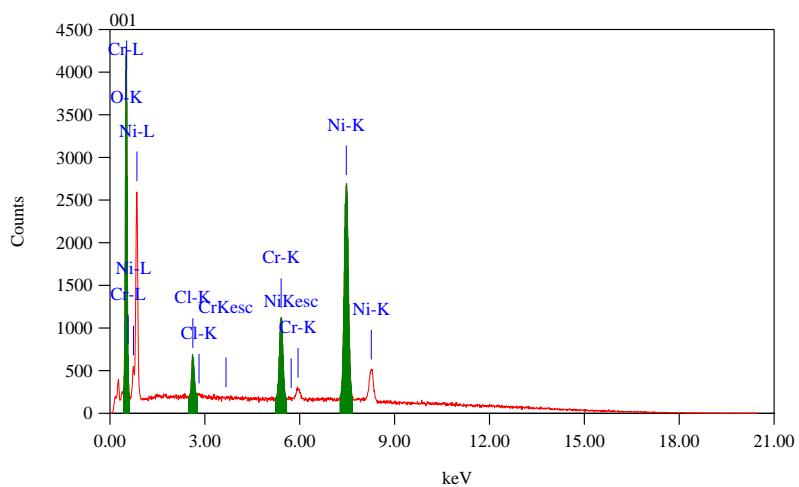
Element	(keV)	Mass%	Sigma	Atom%	Compound	Mass%	Cation	K
Cl K	2.621	2.72	0.04	2.44				2.4633
Cr K	5.411	13.65	0.12	8.37				13.2144
Ni K	7.471	53.45	0.32	29.03				48.7873
O K	0.525	30.18	0.15	60.15				35.5349
Total		100.00		100.00				

Image002



Title : IMG1

Instrument : IT300 (LA)



Acquisition Parameter

Instrument : IT300 (LA)

Acc. Voltage : 20.0 kV

Probe Current : 7.47500 nA

PHA mode : T3

Real Time : 30.00 sec

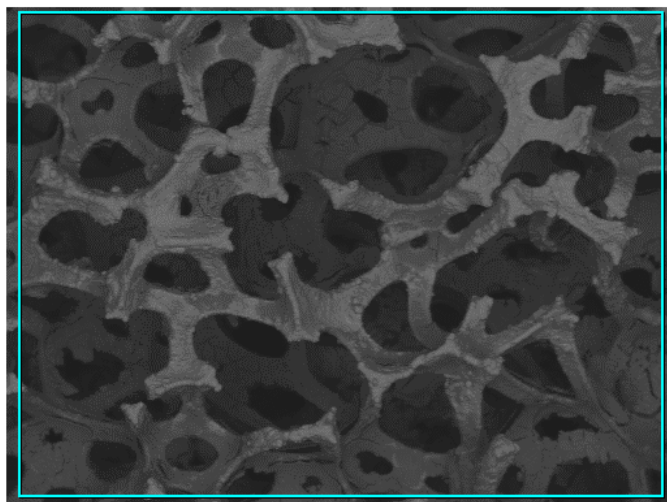
ZAF Method Standardless Quantitative Analysis

Fitting Coefficient : 0.0587

Element	(keV)	Mass%	Sigma	Atom%	Compound	Mass%	Cation	K
Cl K	2.621	2.28	0.04	2.20				2.0666
Cr K	5.411	10.18	0.11	6.70				10.1475
Ni K	7.471	61.75	0.34	35.97				57.7139

Figure S4. EDS spectra of NiCr electrodeposited on NF.

Image000



Title : IMG1

Instrument : IT300 (LA)

Acc. Voltage : 20.0 kV

Probe Current : 7.47500 nA

Acquisition Parameter

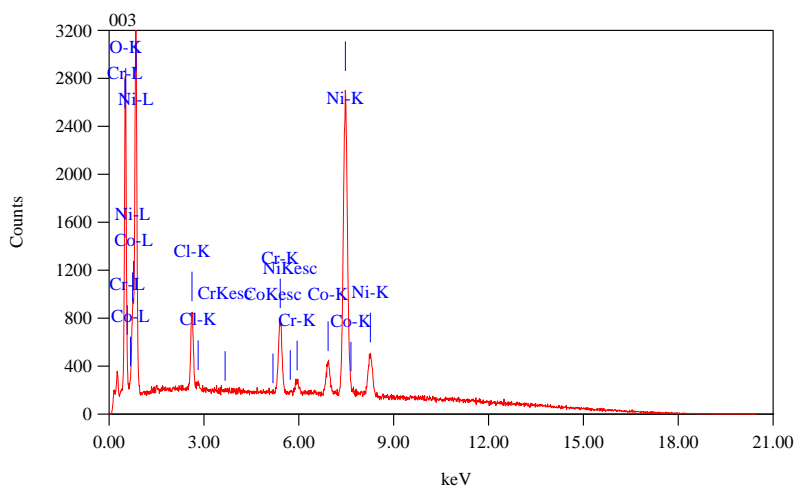
Instrument : IT300 (LA)

Acc. Voltage : 20.0 kV

Probe Current : 7.47500 nA

PHA mode : T3

Real Time : 30.00 sec



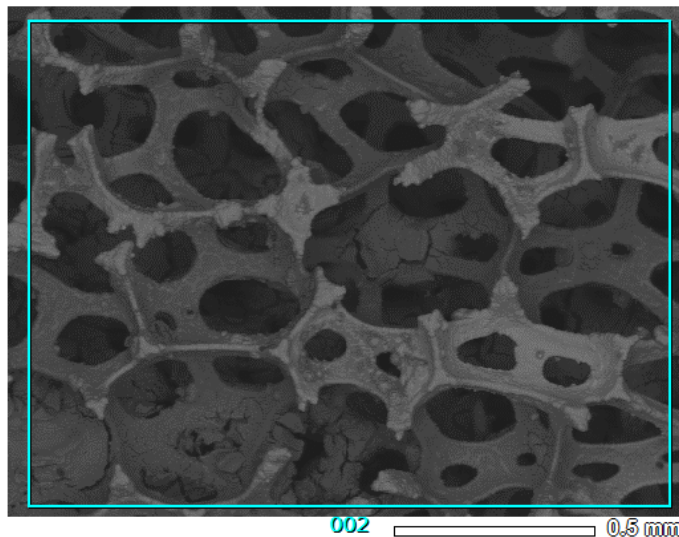
ZAF Method Standardless Quantitative Analysis

Fitting Coefficient : 0.0489

Element	(keV)	Mass%	Sigma	Atom%	Compound	Mass%	Cation	K
Cl K	2.621	3.37	0.05	3.62				3.1125
Co K	6.924	5.68	0.12	3.67				5.2822
Cr K	5.411	6.99	0.10	5.12				7.2515
Ni K	7.471	64.79	0.37	42.01				62.6607
O K	0.525	19.16	0.13	45.59				21.6931
Total		100.00		100.00				

Image001

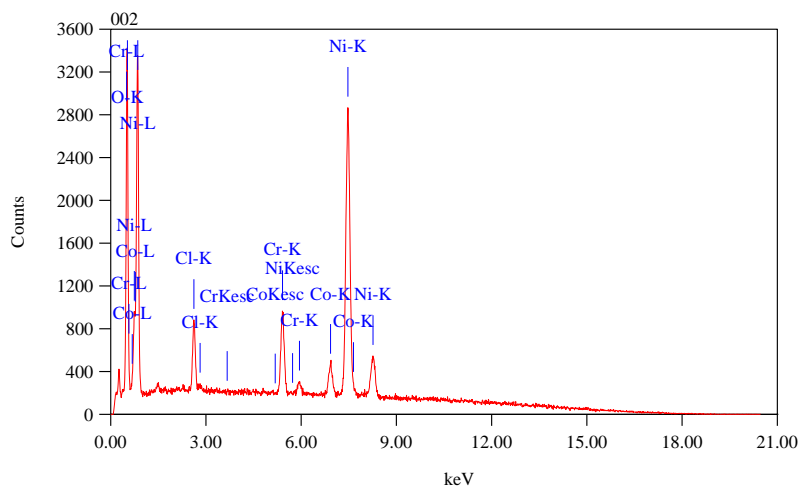
1/1



Title : IMG1

Instrument : IT300 (LA)

Volt : 20.00 kV



Acquisition Parameter

Instrument : IT300 (LA)

Acc. Voltage : 20.0 kV

Probe Current: 7.47500 nA

PHA mode : T3

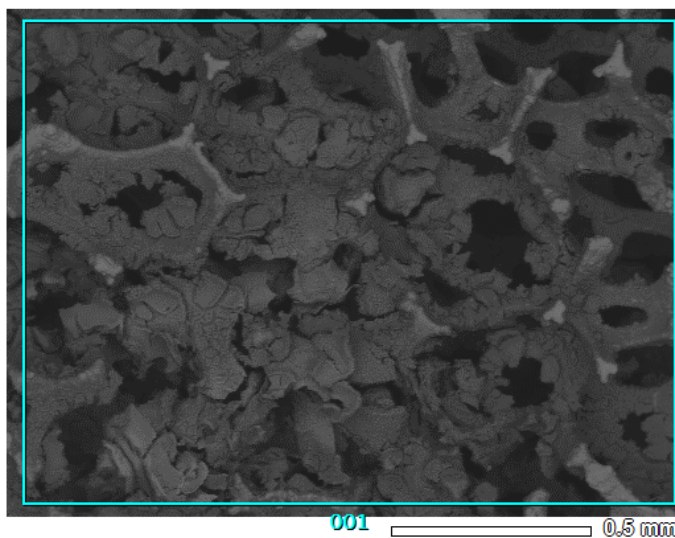
Real Time : 30.00 sec

Live Time : 27.09 sec

ZAF Method Standardless Quantitative Analysis

Fitting Coefficient : 0.0493

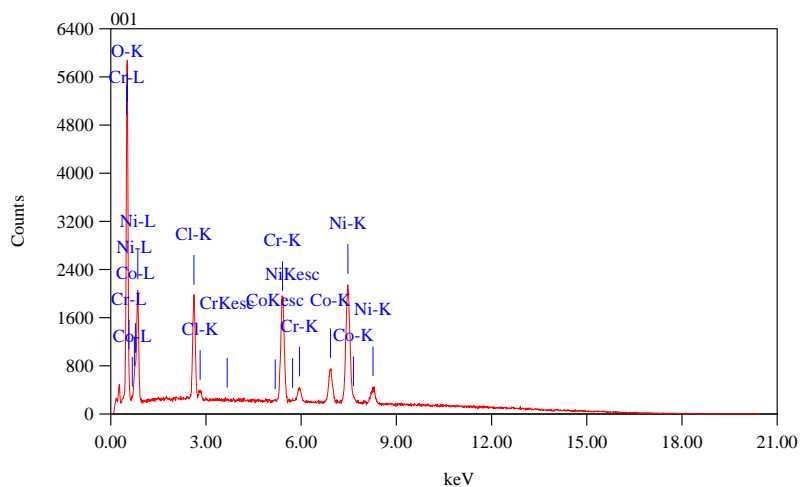
Element	(keV)	Mass%	Sigma	Atom%	Compound	Mass%	Cation	K
Cl K	2.621	3.07	0.05	3.20				2.8241
Co K	6.924	5.51	0.11	3.46				5.0811
Cr K	5.411	7.88	0.10	5.61				8.0999
Ni K	7.471	62.70	0.35	39.52				60.1591
O K	0.525	20.84	0.13	48.21				23.8358
Total		100.00		100.00				



Title : IMG1

Instrument : IT300 (LA)

Volt : 20.00 kV



Acquisition Parameter

Instrument : IT300 (LA)

Acc. Voltage : 20.0 kV

Probe Current: 7.47500 nA

PHA mode : T3

Real Time : 30.00 sec

Live Time : 27.02 sec

ZAF Method Standardless Quantitative Analysis

Fitting Coefficient : 0.0635

Element	(keV)	Mass%	Sigma	Atom%	Compound	Mass%	Cation	K
Cl K	2.621	6.33	0.05	5.61				6.0074
Co K	6.924	9.19	0.12	4.90				8.2070
Cr K	5.411	15.61	0.12	9.43				15.3471
Ni K	7.471	38.60	0.25	20.65				35.9457
O K	0.525	30.26	0.14	59.41				34.4929
Total		100.00		100.00				

Figure S5. EDS spectra of NiCoCr electrodeposited on NF.

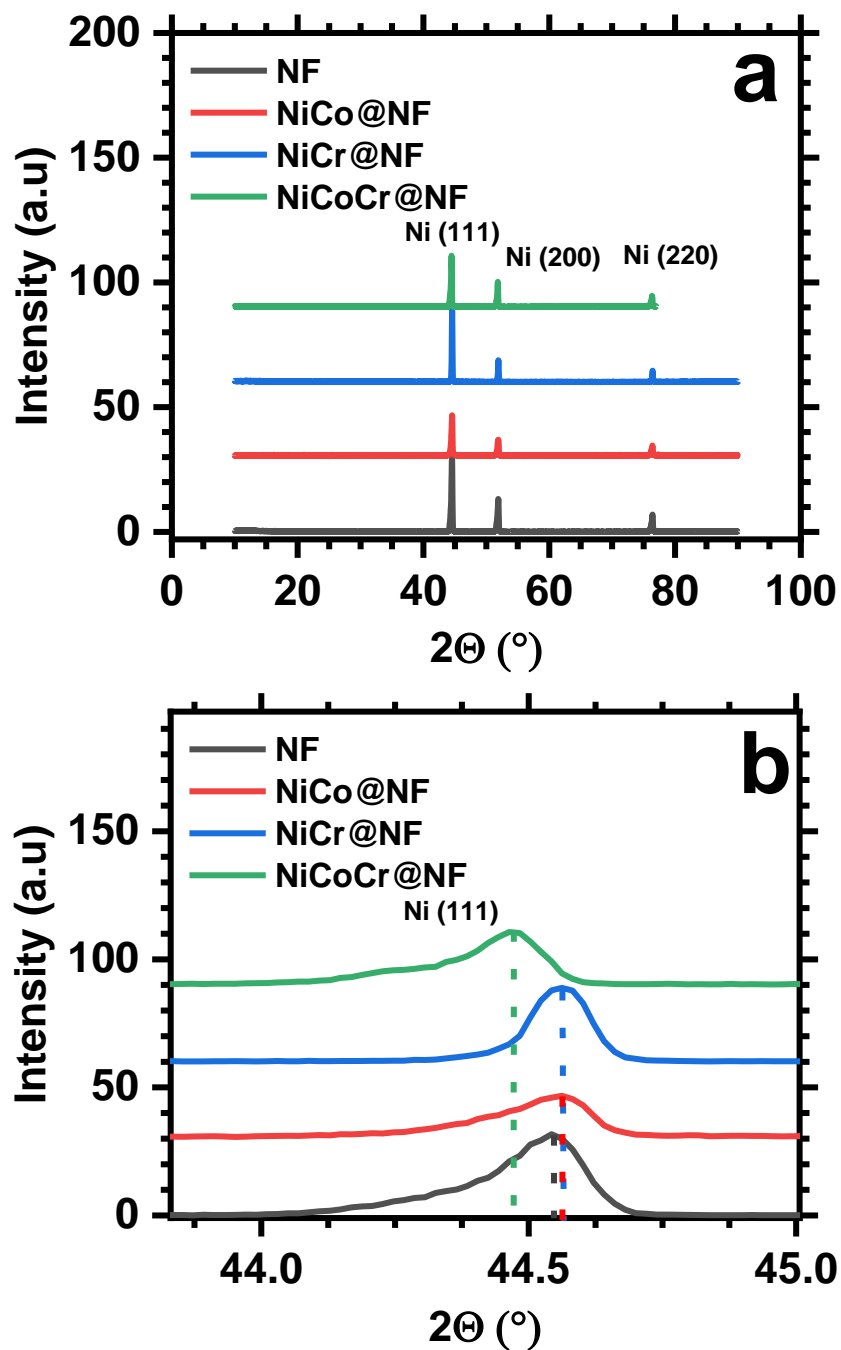


Figure S6. (a) XRD patterns of bare NF, NiCo, NiCr, and NiCoCr electrodeposited on NF. (b) Zoom on the Ni(111) peak.

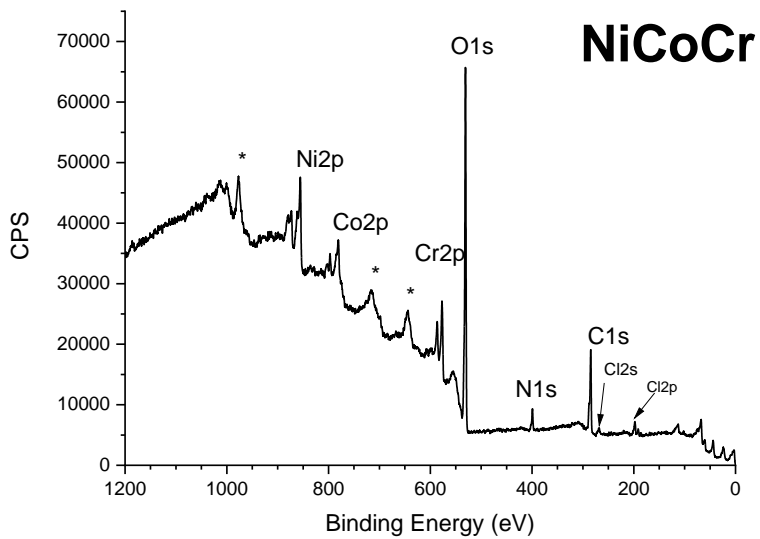
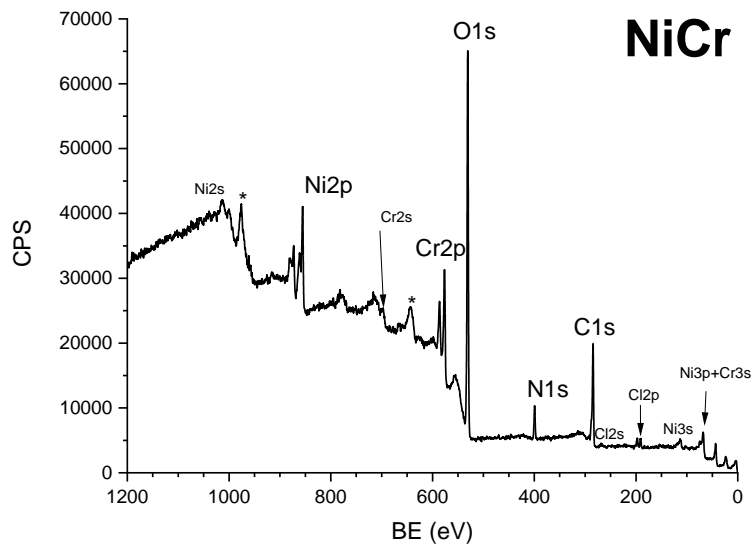
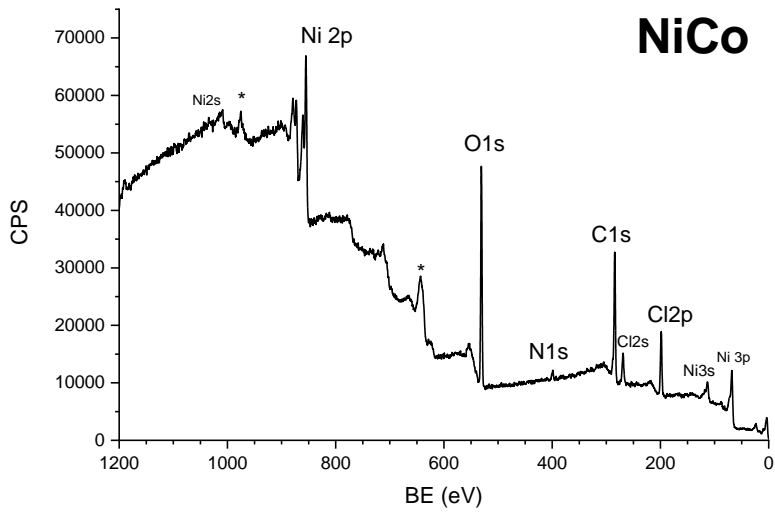


Figure S7. XPS survey spectra for the three metallic alloys electrodeposited on NF. *The peaks indicated by asterisks are Auger peaks.*

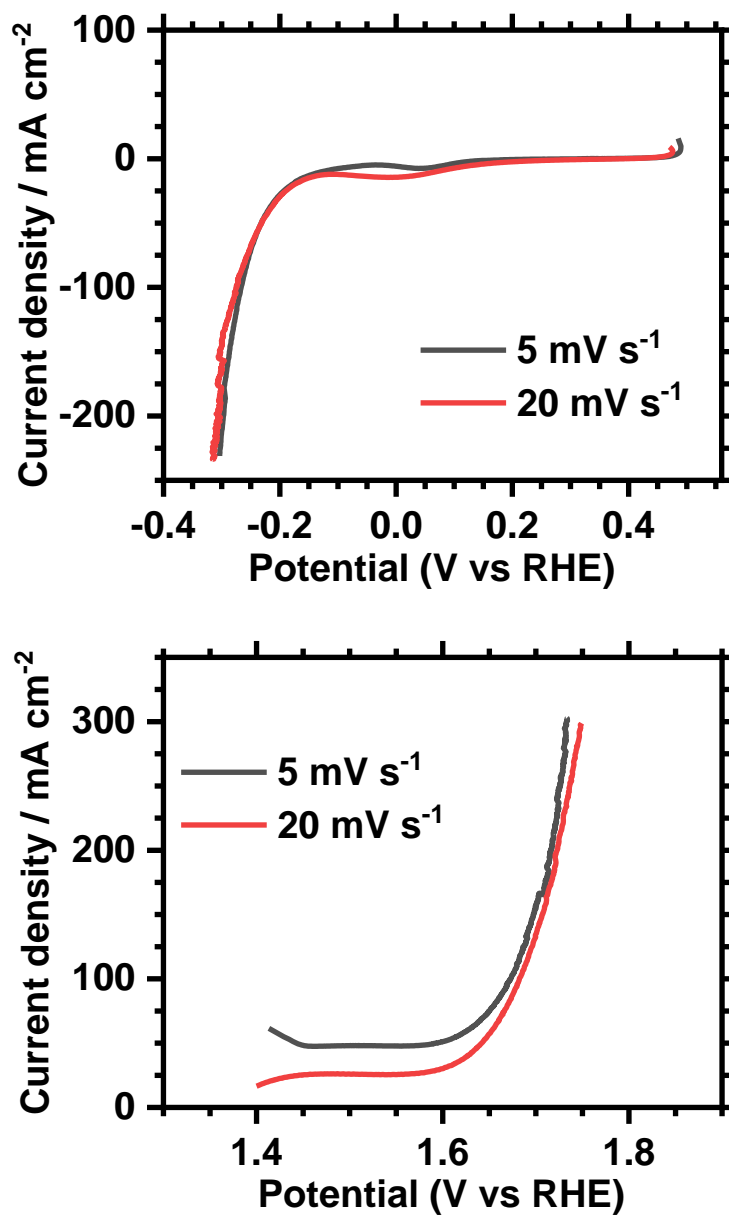


Figure S8. Linear sweep voltammograms of NiCoCr electrodeposited on NF at 5 and 20 mV/s in 1M KOH.

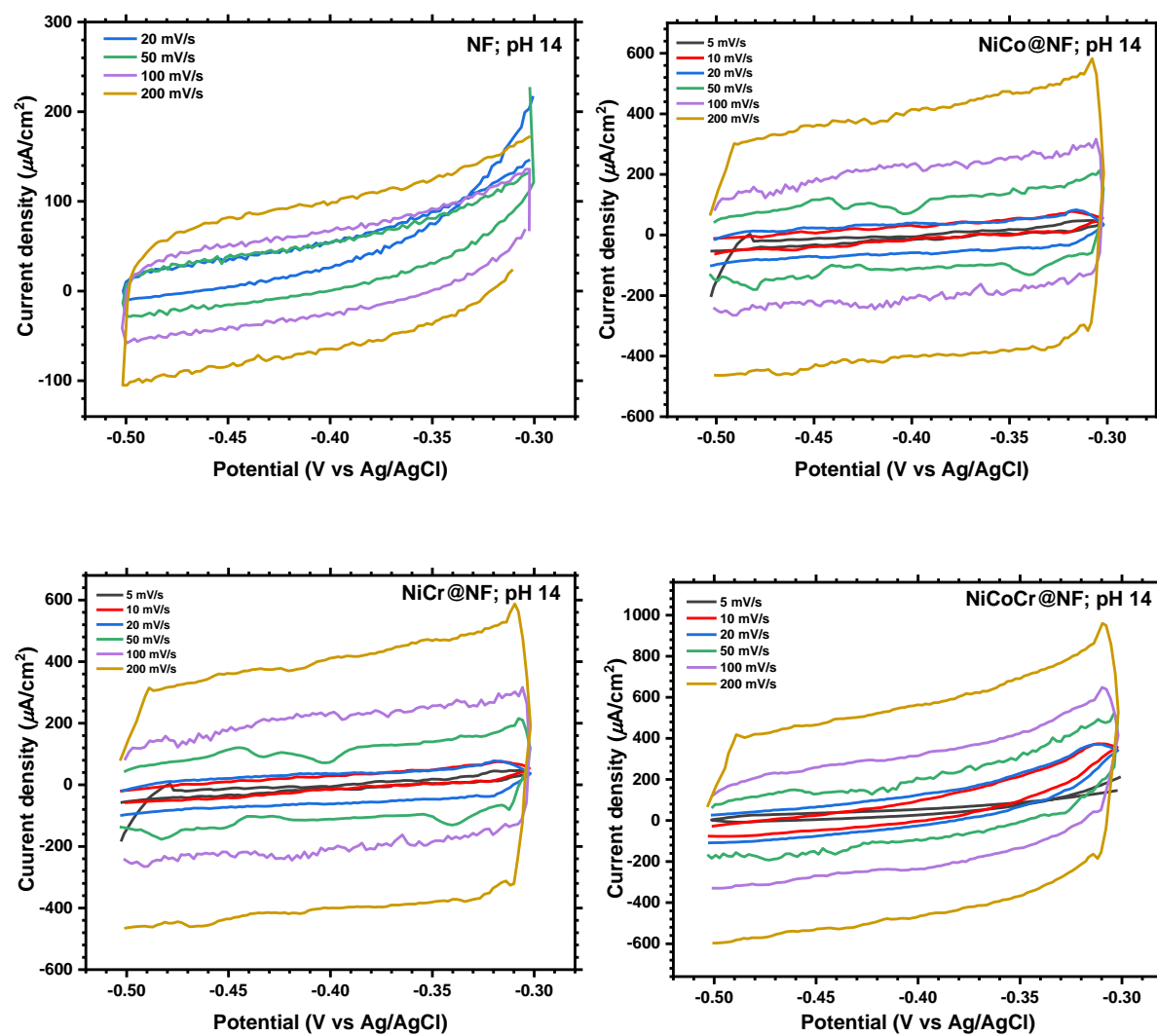


Figure S9. Cyclic voltammograms in a non-Faradaic region at different scan rates for bare NF, NiCo, NiCr and NiCoCr in 1 M KOH.

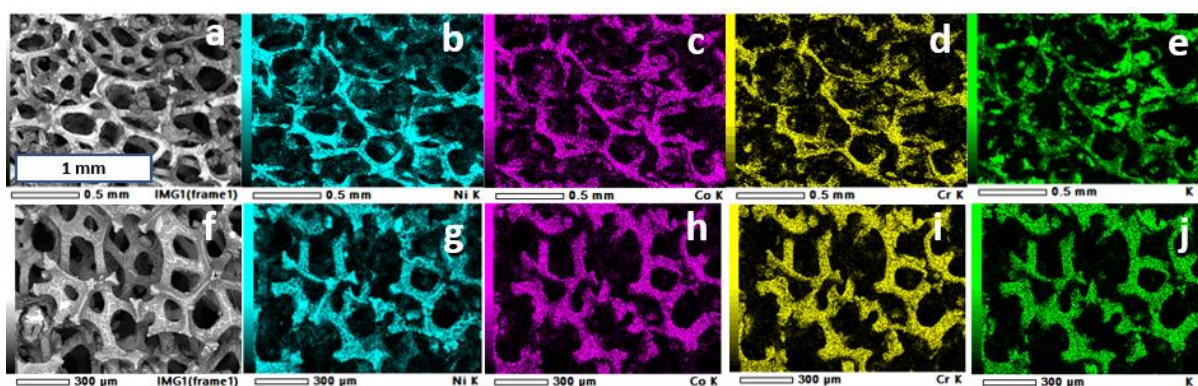


Figure S10. EDS mapping of NiCoCr after 10 h electrolysis at +100 mA cm⁻² (a-e) and -100 mA cm⁻² (f-j) showing the homogeneous distribution of Ni (b,g, blue), Co (c,h, pink), Cr (d,i, yellow) and K (e,j, green). The potassium deposit comes from the KOH electrolyte.

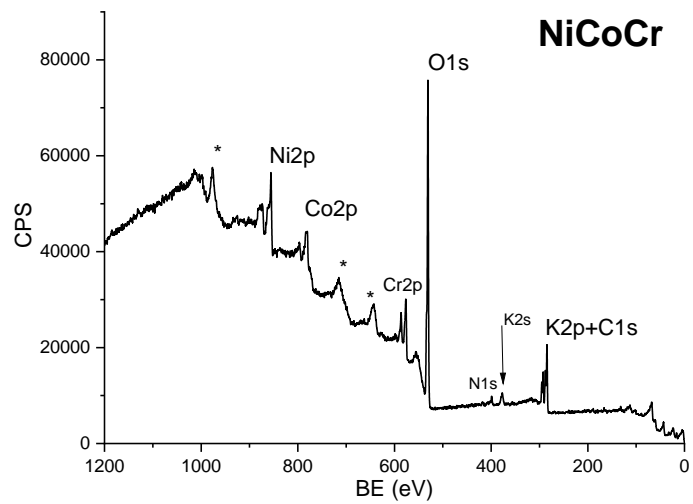
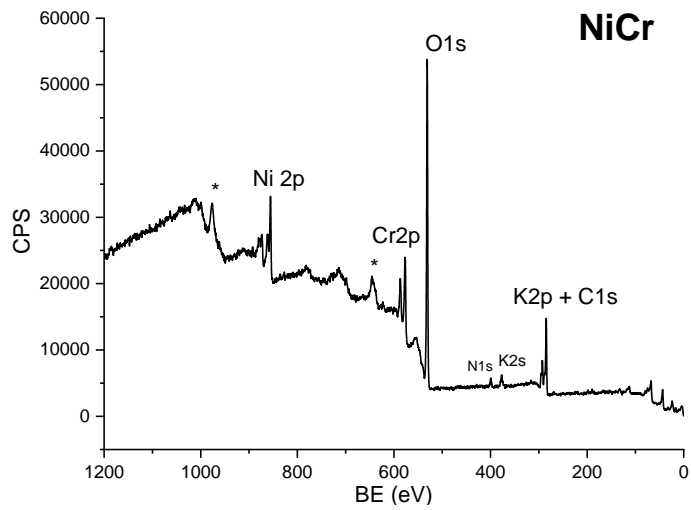
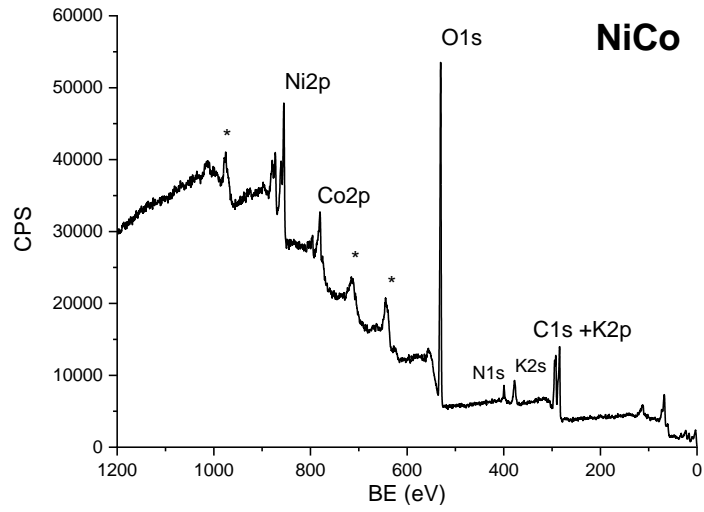


Figure S11. XPS survey spectra for the three metallic alloys after the electrolytic test at -70 mA cm^{-2} for 10 h. *The peaks indicated by asterisks correspond to Auger peaks.*

Table S1. Optimized composition and concentration of electrolytic baths (in mM) for electrodepositing NiCo, NiCr and NiCoCr on nickel foam (NF).

Reagent	NiCo	NiCr	NiCoCr
NiCl ₂	50	50	50
CoCl ₂	12	-	12
CrCl ₃	-	28	28
NH ₂ CH ₂ CH ₂ NH ₂ ·2HCl	30	30	30
H ₃ BO ₃	50	50	50

Table S2. Atomic ratios for the metallic species determined from XPS survey spectra.

Material		Ni/O	Co/Ni	Cr/Ni
NiCo	<i>before electrolysis</i>	0.26	0.73	-
	<i>after electrolysis^a</i>	0.20	0.61	-
NiCr	<i>before electrolysis</i>	0.13	-	1.26
	<i>after electrolysis^a</i>	0.12	-	1.36
NiCoCr	<i>before electrolysis</i>	0.14	0.74	0.88
	<i>after electrolysis^a</i>	0.13	0.91	0.84

^a At -70 mA cm^{-2} for 10h.

Table S3. XPS fitting parameters for Ni2p_{3/2} before and after HER electrolysis^a

		Ni(OH) ₂	NiCl ₂	other	Inter-band	Satell. 1	Satell. 2	Satell. 2
NiCo <i>before</i>	BE (eV)	855.4	856.7	-	858.0	860.6	863.1	866.1
	FWHM (eV)	2.05	2.07		1.98	3.1	3.5	3.5
	Contribution (%)	39.4	10.5		7.1	22.0	15.6	5.4
NiCo <i>after</i>	BE (eV)	855.6	-	852.5 (Ni ⁰)	857.8	860.7	863.1	866.05
	FWHM (eV)	2.7		2.2	2.4	3.2	3.8	3.1
	Contribution (%)	46.7		2.3	9.2	25.8	13.7	2.6
NiCr <i>before</i>	BE (eV)	855.6	856.7	-	858.2	860.9	863.5	866.3
	FWHM (eV)	2.1	2.3		2.6	3.6	3.5	3.6
	Contribution (%)	22.1	16.0		14.8	23.1	16.7	7.3
NiCr	BE (eV)	855.7	856.9		858.4	860.9	863.3	866.0

<i>after</i>	FWHM (eV)	2.1	2.3		2.3	3.1	3.5	3.7
	Contribution (%)	39.8	10.7		11.0	18.8	15.5	4.2
NiCoCr	BE (eV)	855.7	856.8	857.5 (Ni ³⁺)	858.5	860.9	863.9	866.1
<i>before</i>	FWHM (eV)	1.9	2.3	2.9	3.1	4.2	3.3	3.9
	Contribution (%)	21.6	5.8	9.4	15.2	25.8	12.4	9.8
NiCoCr	BE (eV)	855.6	-	857.5 (Ni ³⁺)	858.1	860.7	863.2	866.2
<i>after</i>	FWHM (eV)	2.2		2.5	3.0	3.7	3.9	3.5
	Contribution (%)	34.5		5.0	14.3	21.7	18	6.5

^a At -70 mA cm⁻² for 10h.

Table S4. XPS fitting parameters for Co2p_{3/2} and Cr2p_{3/2} before and after HER electrolysis^a

NiCo		NiCr		NiCoCr	
<i>before</i>	<i>after</i>	<i>before</i>	<i>after</i>	<i>before</i>	<i>after</i>

Co2p_{3/2}					
BE (eV)	780.7	780.6	780.9	780.7	
Contribution (%)	42.7	39.1	37.0	33.1	
BE (eV)	782.5	782.5	782.8	782.8	
Contribution (%)	24.3	31.7	20.0	12.6	
BE (eV)	785.8	786.2	785.9	785.2	
Contribution (%)	29.4	27.5	33.8	34.8	
BE (eV)	790.4	790.5	789.4	789.8	
Contribution (%)	3.6	1.7	9.2	12.6	
Cr2p_{3/2}		<u>Cr₂O₃</u>			
BE (eV)		576.7	576.5	576.5	576.6
Contribution (%)		29.8	37.0	30.4	42.0
		<u>Cr(OH)₂</u>			
BE (eV)		578.1	577.6	577.7	577.6
Contribution (%)		58.1	52.7	37.0	35.4
		<u>Cr(VI)</u>			
BE (eV)		580.5	579.9	580.1	580.0
Contribution (%)		12.1	10.3	32.6	22.6

^a At -70 mA cm⁻² for 10h.

Table S5. Comparison of the HER activity of NiCo, NiCr and NiCoCr electrodeposited on nickel foam (@NF) with that of other Ni-based bi- and trimetallic electrocatalysts reported in the literature.

Catalyst ^{ref}	Electrolyte	η_{-10} / V	η_{+10} / V
NiCo@NF ^{This work}	1 M KOH	0.20	0.39
NiCr@NF ^{This work}	1 M KOH	0.10	0.45
NiMo@GC ^[S1]	1M KOH	0.28	0.30
NiFe@Cu ^[S2]	1 M KOH	0.13	0.34
NiCoMo@GC ^[S1]	1 M KOH	0.05	0.20
NiCoCr@NF ^{This work}	1 M KOH	0.11	0.37
NiFeCr@CP ^[S3]	1 M KOH	/	0.28
NiCoFe@Cu ^[S2]	1 M KOH	0.09	0.32
NiMoCr ^[S4]	1 M KOH	0.25	/
NiFeMo@NF ^[S5]	1M KOH	0.03	0.20

CP: Carbon paper; GC: glassy carbon electrode.

with the corresponding references:

[S1] Jeghan, S. M. N.; Kim, N.; Lee, G. Mo-Incorporated Three-Dimensional Hierarchical Ternary Nickel-Cobalt-Molybdenum Layer Double Hydroxide for High-Efficiency Water Splitting. *Int. J. Hydrog. Energy* **2021**, *46* (43), 22463–22477. <https://doi.org/10.1016/j.ijhydene.2021.04.071>

[S2] Barati Darband, Gh.; Aliofkhaezrai, M.; Rouhaghdam, A. S. Facile Electrodeposition of Ternary Ni-Fe-Co Alloy Nanostructure as a Binder Free, Cost-Effective and Durable Electrocatalyst for High-Performance Overall Water Splitting. *J. Colloid Interface Sci.* **2019**, *547*, 407–420. <https://doi.org/10.1016/j.jcis.2019.03.098>.

[S3] Yang, Y.; Dang, L.; Shearer, M. J.; Sheng, H.; Li, W.; Chen, J.; Xiao, P.; Zhang, Y.; Hamers, R. J.; Jin, S. Highly Active Trimetallic NiFeCr Layered Double Hydroxide Electrocatalysts for Oxygen Evolution Reaction. *Adv. Energy Mater.* **2018**, *8* (15), 1703189. <https://doi.org/10.1002/aenm.201703189>.

[S4] Nady, H.; El-Rabiei, M. M.; Samy, M.; Deyab, M. A.; Abd El-Hafez, G. M. Novel Ni–Cr-Based Alloys as Hydrogen Fuel Sources through Alkaline Water Electrolytes. *Int. J. Hydrog. Energy* **2021**, *46* (70), 34749–34766. <https://doi.org/10.1016/j.ijhydene.2021.08.056>.

[S5] Hsieh, C.-T.; Huang, C.-L.; Chen, Y.-A.; Lu, S.-Y. NiFeMo Alloy Inverse-Opals on Ni Foam as Outstanding Bifunctional Catalysts for Electrolytic Water Splitting of Ultra-Low Cell Voltages at High Current Densities. *Appl. Catal. B Environ.* **2020**, *267*, 118376. <https://doi.org/10.1016/j.apcatb.2019.118376>.