Supplementary Information

Rationally engineered high-entropy oxides using finely tunable combustion synthesis for Li-ion battery anodes

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Equation S1. Chemical Balanced Equation with glycine at various fuel to oxidizer ratio

(i) $\varphi = 0.9$

$$0.862C_2H_5NO_2 + 0.2Mn(NO_3)_2{\cdot}4H_2O + 0.2Fe(NO_3)_3{\cdot}9H_2O + 0.2Co(NO_3)_2{\cdot}6H_2O + 0.2Cu(NO_3)_2{\cdot}3H_2O + 0.2Ni(NO_3)_2{\cdot}6H_2O \rightarrow 0.0527Mn(NO_3)_2{\cdot}4H_2O + 0.0527Fe(NO_3)_3{\cdot}9H_2O + 0.0527Co(NO_3)_2{\cdot}6H_2O + 0.0527Cu(NO_3)_2{\cdot}3H_2O + 0.0527Ni(NO_3)_2{\cdot}6H_2O + 6.263H_2O + 1.724CO_2 + 1.531N_2 + 0.246(MnFeCoNiCu)_3O_4$$

(ii) $\varphi = 0.95$

$$1.013C_2H_5NO_2 + 0.2Mn(NO_3)_2{\cdot}4H_2O + 0.2Fe(NO_3)_3{\cdot}9H_2O + 0.2Co(NO_3)_2{\cdot}6H_2O + 0.2Cu(NO_3)_2{\cdot}3H_2O + 0.2Ni(NO_3)_2{\cdot}6H_2O \rightarrow 0.027Mn(NO_3)_2{\cdot}4H_2O + 0.027Fe(NO_3)_3{\cdot}9H_2O + 0.027Co(NO_3)_2{\cdot}6H_2O + 0.027Cu(NO_3)_2{\cdot}3H_2O + 0.027Ni(NO_3)_2{\cdot}6H_2O + 7.377H_2O + 2.026CO_2 + 1.61N_2 + 0.288(MnFeCoNiCu)_3O_4$$

(iii) $\varphi = 1.0$

$$1.17C_2H_5NO_2 + 0.2Mn(NO_3)_2{\cdot}4H_2O + 0.2Fe(NO_3)_3{\cdot}9H_2O + 0.2Co(NO_3)_2{\cdot}6H_2O + 0.2Cu(NO_3)_2{\cdot}3H_2O + 0.2Ni(NO_3)_2{\cdot}6H_2O \rightarrow 8.527H_2O + 2.34CO_2 + 1.685N_2 + 0.333(MnFeCoNiCu)_3O_4$$

(iv) $\varphi = 1.05$

$$1.336C_2H_5NO_2 + 0.2Mn(NO_3)_2{\cdot}4H_2O + 0.2Fe(NO_3)_3{\cdot}9H_2O + 0.2Co(NO_3)_2{\cdot}6H_2O + 0.2Cu(NO_3)_2{\cdot}3H_2O + 0.2Ni(NO_3)_2{\cdot}6H_2O \rightarrow 0.166C_2H_5NO_2 + 8.527H_2O + 2.34CO_2 + 1.685N_2 + 0.333(MnFeCoNiCu)_3O_4$$

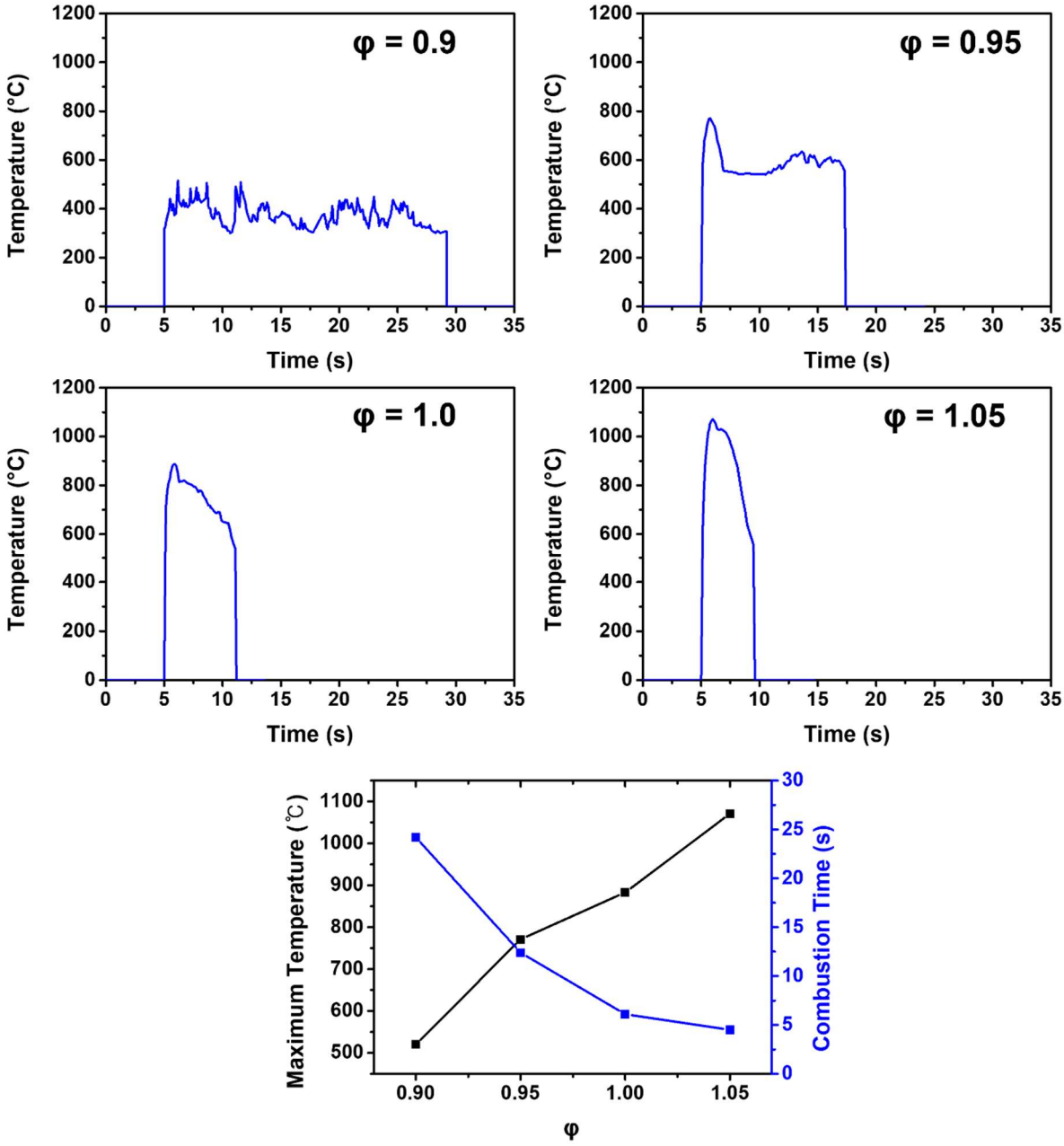


Figure S1. Real-time temperature profiles during combustion synthesis. As the fuel to oxidizer ratios increase from φ-0.9, φ-0.95, φ-1, to φ-1.05, the temperature rises while the sustained time decreases.

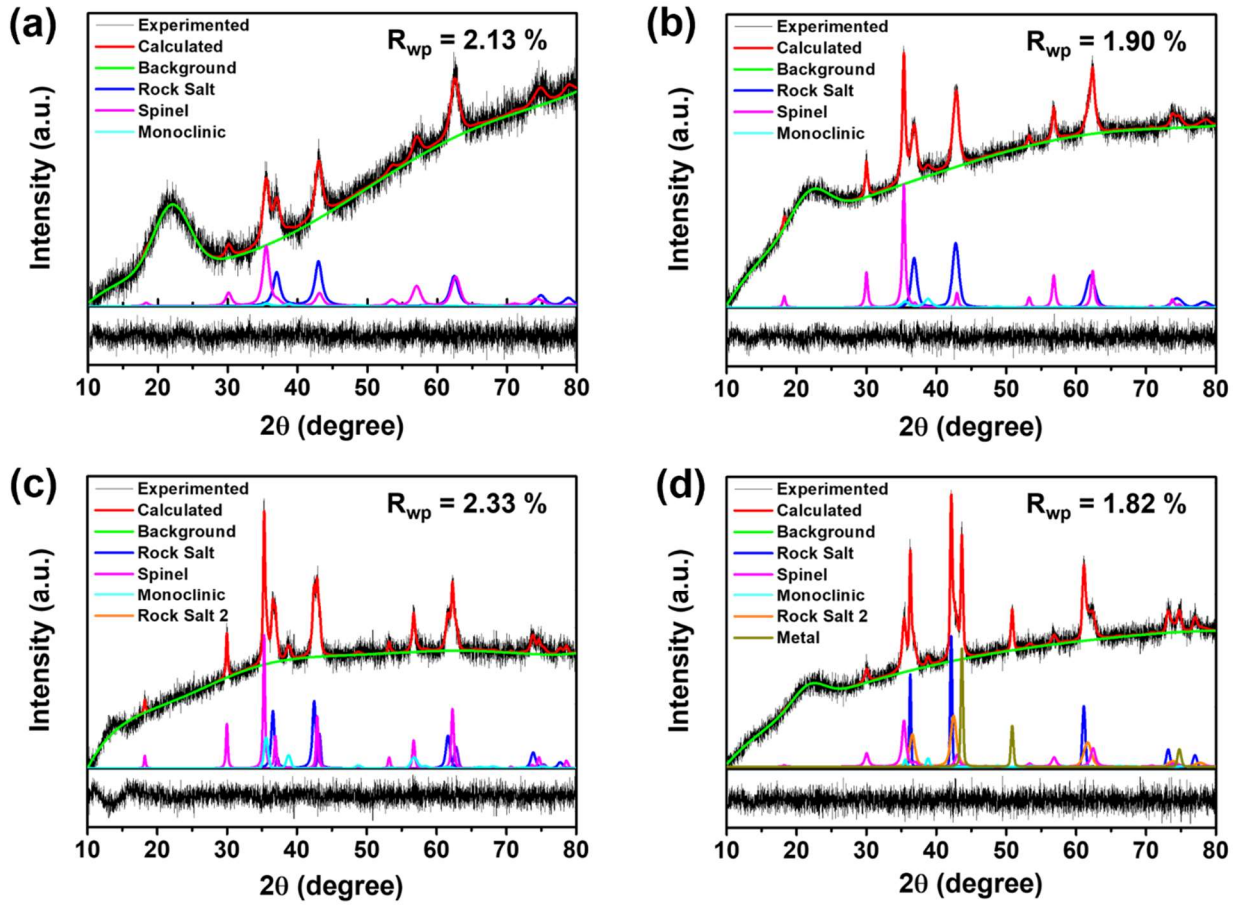
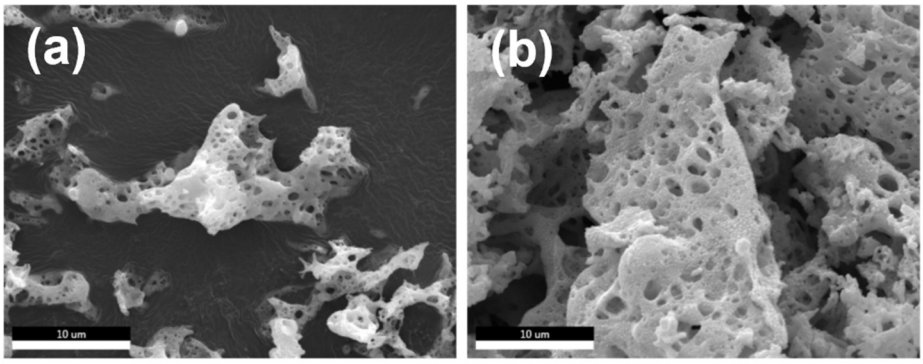
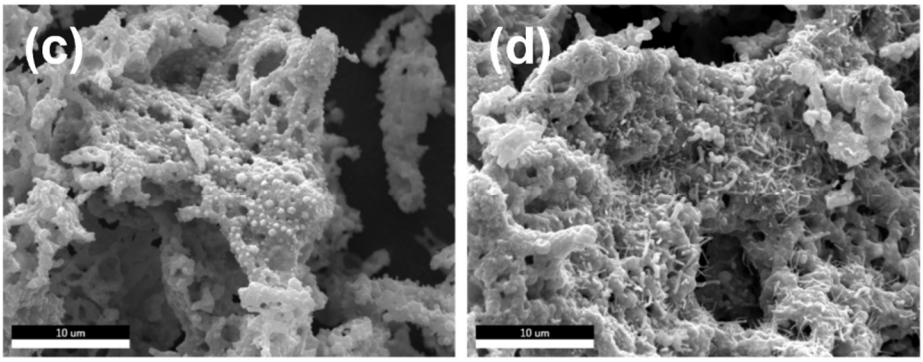


Figure S2. XRD patterns and quantitative analyses using Rietveld refinement method. Experimentally measured XRD spectrums and calculated patterns of fabricated HEO composites using different fuel to oxidizer ratios of (a) φ-0.9, (b) φ-0.95, (c) φ-1, and (d) φ-1.05.



Element	Weight %	Atomic %
O K	23.70	53.21
Mn K	15.22	9.95
Fe K	12.65	8.14
Co K	14.63	8.91
Ni K	14.58	8.92
Cu K	19.22	10.86

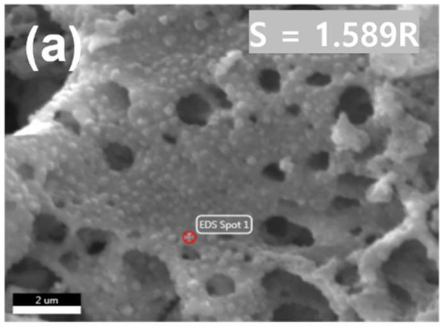
Element	Weight %	Atomic %
O K	19.74	47.12
Mn K	18.11	12.59
Fe K	16.54	11.31
Co K	15.88	10.29
Ni K	16.22	10.55
Cu K	13.52	8.13



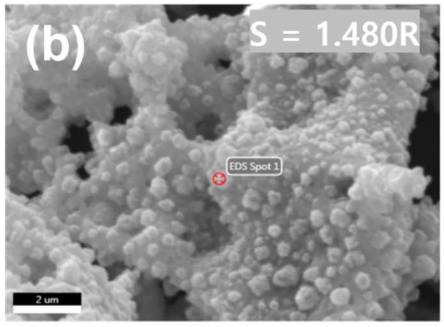
Element	Weight %	Atomic %
O K	18.25	44.87
Mn K	18.13	12.98
Fe K	14.95	10.53
Co K	15.21	10.15
Ni K	14.93	10.00
Cu K	18.53	11.47

Element	Weight %	Atomic %
O K	18.98	45.88
Mn K	19.27	13.57
Fe K	16.44	11.38
Co K	16.94	11.12
Ni K	15.72	10.36
Cu K	12.65	7.70

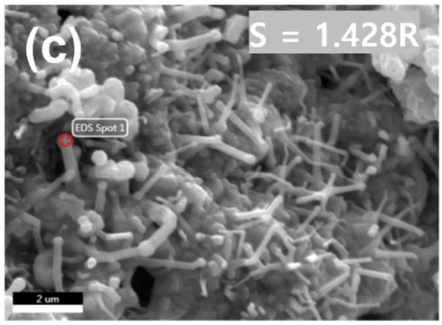
Figure S3. Scanning electron microscopy (SEM) images and corresponding areal EDS analyses for investigating the elemental distribution in the fabricated HEO composites using different fuel to oxidizer ratios of (a) φ-0.9, (b) φ-0.95, (d) φ-1, and (d) φ-1.05.



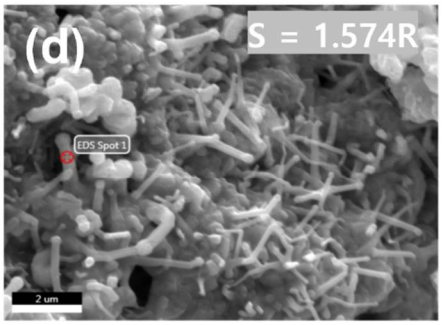
Element	Weight %	Atomic %
O K	17.78	44.31
Mn K	14.94	10.83
Fe K	14.51	10.35
Co K	14.21	9.61
Ni K	13.47	9.15
Cu K	25.06	15.72



Element	Weight %	Atomic %
O K	17.92	44.92
Mn K	11.84	8.64
Fe K	11.26	8.08
Co K	11.59	7.89
Ni K	10.45	7.14
Cu K	36.91	23.29

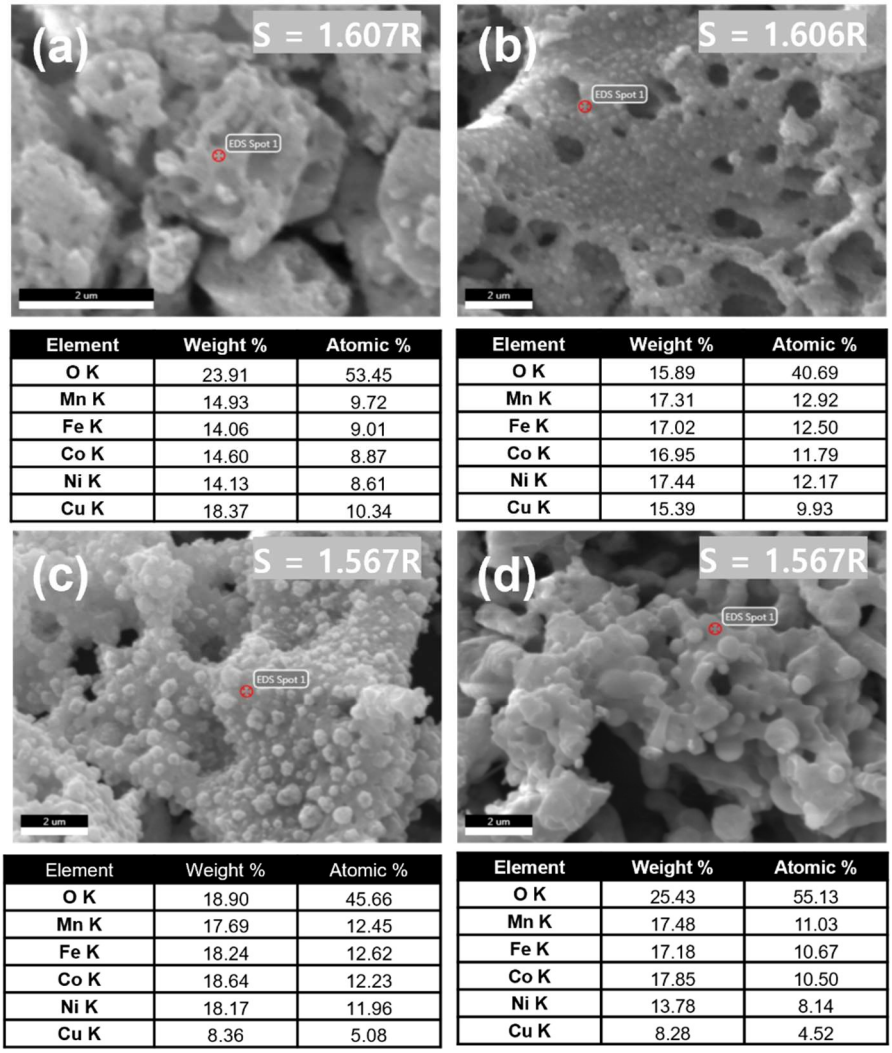


Element	Weight %	Atomic %
O K	17.06	43.55
Mn K	11.97	8.90
Fe K	9.56	6.99
Co K	9.24	6.40
Ni K	11.37	7.91
Cu K	40.81	26.24



Element	Weight %	Atomic %
O K	21.47	49.64
Mn K	19.44	13.08
Fe K	17.35	11.49
Co K	17.82	11.18
Ni K	14.24	8.97
Cu K	9.67	5.63

Figure S4. Point EDS mapping analyses of spherical nanoparticles and nanorods in HEO composites for examining the elemental distribution and configurational entropy calculated from cation ratios. SEM images of analyzed points and elemental distribution from the point EDS analysis of the spherical nanoparticles in the fabricated HEO composites using fuel to oxidizer ratios of (a) φ-0.95, (b) φ-1.0, and (c) φ-1.05. (d) SEM image of the analyzed point and elemental distribution from the point EDS analysis of the middle of a nanorod in the fabricated HEO composites using a fuel to oxidizer ratio of φ-1.05.



Element	Weight %	Atomic %
O K	23.91	53.45
Mn K	14.93	9.72
Fe K	14.06	9.01
Co K	14.60	8.87
Ni K	14.13	8.61
Cu K	18.37	10.34

Element	Weight %	Atomic %
O K	15.89	40.69
Mn K	17.31	12.92
Fe K	17.02	12.50
Co K	16.95	11.79
Ni K	17.44	12.17
Cu K	15.39	9.93

Element	Weight %	Atomic %
O K	18.90	45.66
Mn K	17.69	12.45
Fe K	18.24	12.62
Co K	18.64	12.23
Ni K	18.17	11.96
Cu K	8.36	5.08

Element	Weight %	Atomic %
O K	25.43	55.13
Mn K	17.48	11.03
Fe K	17.18	10.67
Co K	17.85	10.50
Ni K	13.78	8.14
Cu K	8.28	4.52

Figure S5. Point EDS mapping analyses of non-spherical regimes in HEO composites for examining the elemental distribution and configurational entropy calculated from the cation ratios. SEM images of analyzed points and elemental distribution from the point EDS analysis of non-spherical regimes in the fabricated HEO composites using fuel to oxidizer ratios of (a) φ-0.9, (b) φ-0.95, (c) φ-1.0, and (d) φ-1.05.

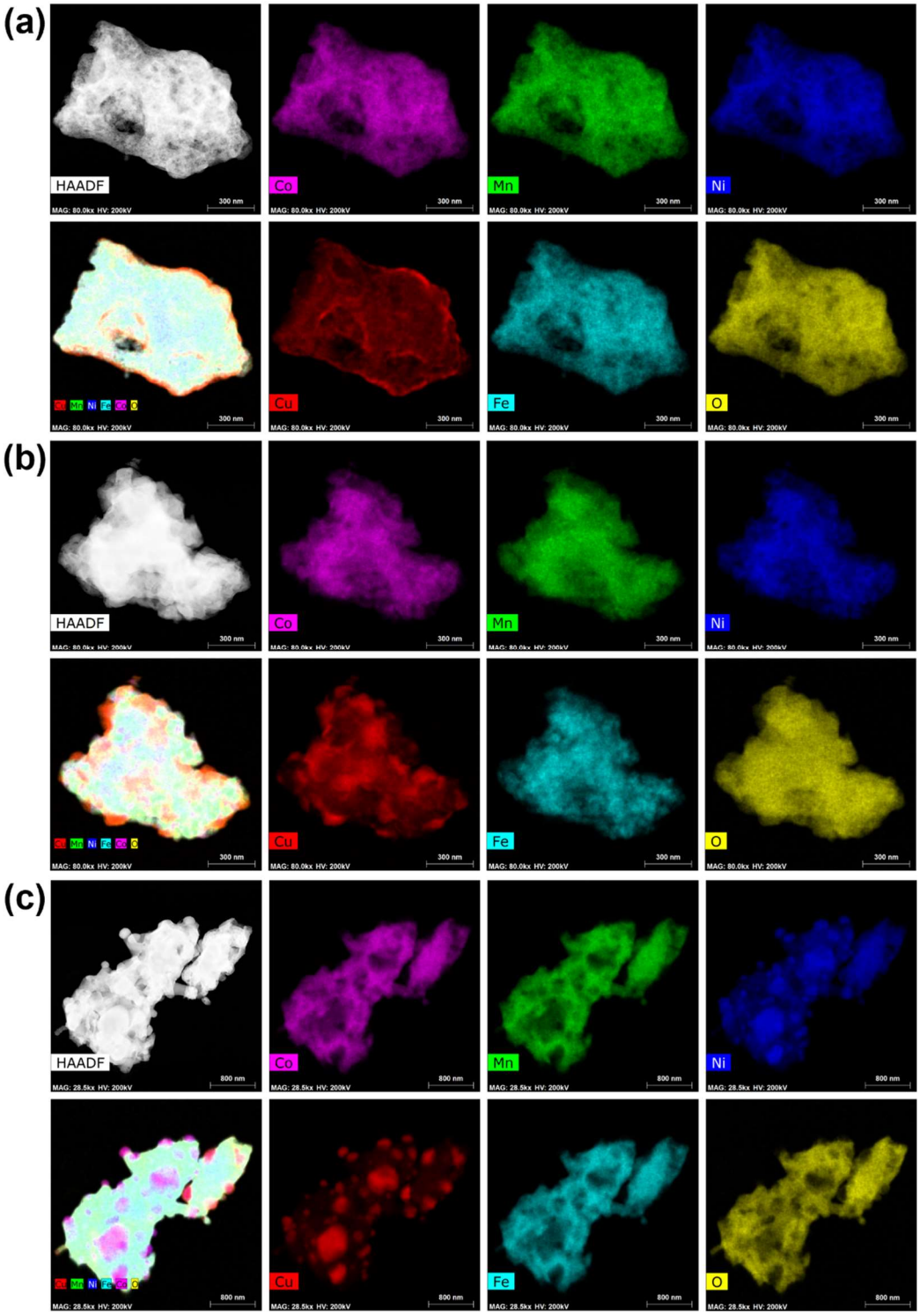


Figure S6. High-resolution TEM and EDS mapping images of HEO composites, fabricated with (a) φ-0.9, (b) φ-1.0, and (c) φ-1.05. Homogeneously distributed metal and oxygen elements are observed, while a partial separation of Cu appears.

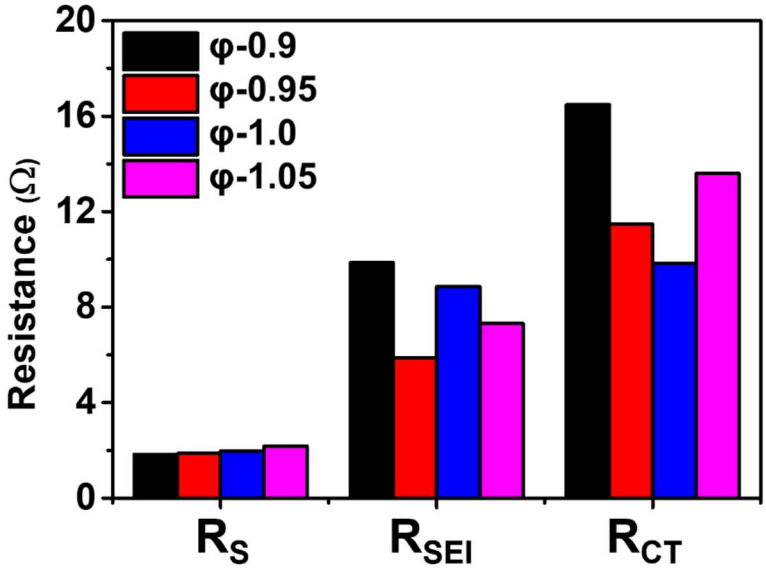


Figure S7. Fitted resistances using the equivalent circuit model based on electrochemical impedance spectroscopy (EIS) analysis.

Table S1. Calculated phase volume fractions based on Rietveld refinement of fabricated HEO composites using different fuel to oxidizer ratios (φ-0.9, φ-0.95, φ-1, and φ-1.05).

Phase Volume Fraction					
φ	Spinel (%)	Rock Salt (%)	Monoclinic (%)	Metal (%)	Rock Salt 2 (%)
0.9	58.08	39.82	2.1		
0.95	56.97	39.15	3.87		
1	53.45	32.16	7.53		6.86
1.05	25.96	31.21	1.98	12.34	28.51

Cell Parameter (Å)								
φ	Spinel	Rock Salt	Metal	Rock Salt 2	Monoclinic			
	a	a	a	a	a	b	c	β
0.9	8.386	4.207	-		4.693	3.428	5.100	99.546
0.95	8.421	4.229	-		4.693	3.428	5.100	99.546
1	8.432	4.257	-	4.185	4.693	3.428	5.100	99.546
1.05	8.416	4.290	3.591	4.256	4.693	3.428	5.100	99.546

Grain Size (nm)					
φ	Spinel	Rock Salt	Monoclinic	Metal	Rock Salt 2
0.9	11.7	9.2	10	-	
0.95	24.5	18.2	8.9	-	
1	41.1	22.4	70.0	-	53.3
1.05	23.5	170.4	70.0	56.4	16.6