Deeper Understanding of Ternary Eutectic Carbonates/Ceria-based Oxide Composite Electrolyte through Thermal Cycling

-SUPPLEMENTARY INFORMATION-

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1. Chromatographic analysis of the outlet gas mixture during EIS thermal cycling analysis

To perform the output gas analysis during a thermal cycling of composite electrolyte SDC-LiNaK under MCFC standard reducing atmosphere a GC Trace 1310™ (Thermo Fisher Scientific) was used according to the scheme and protocol established by Meskine *et al.* [1]. A two column setup with a Thermal Conductivity Detector (TCD) was adopted to perform a separation of gases. The results are presented in figure S1 as a spectrum of electrical signal as function of retention times at two different temperatures. The retention time values for detected gases are summarized in Table S1.

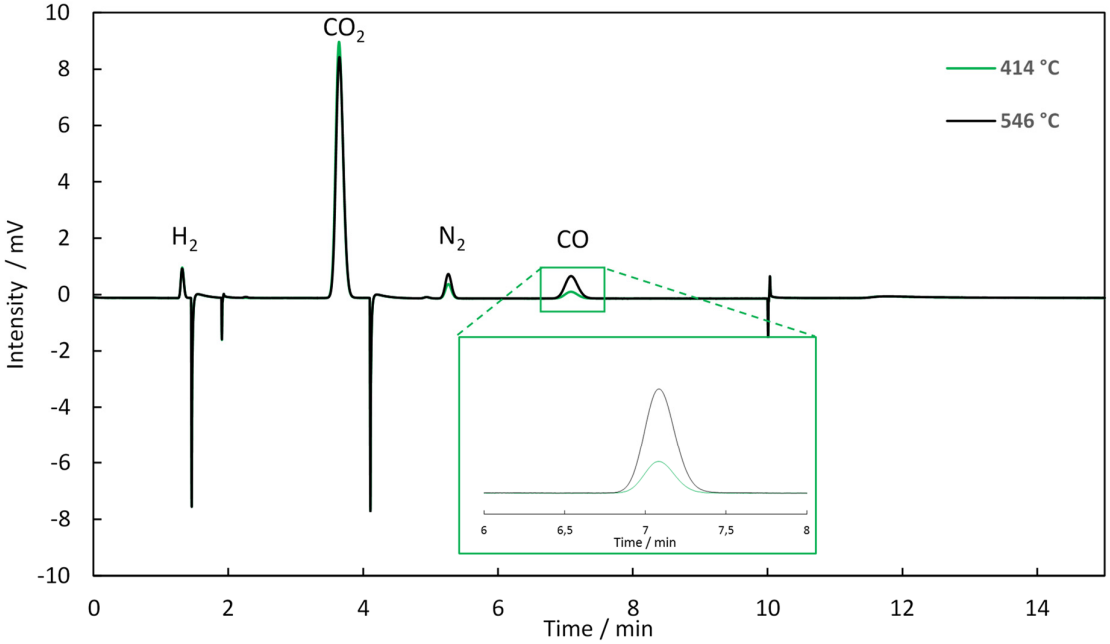

Figure S1. Outlet composition of gas mixture during EIS thermal cycling analysis of SDC-

LiNaK under MCFC standard reducing conditions at 441°C and 546°C.

Table S1. Retention times of gases forming an outlet mixture during EIS thermal cycling analysis of SDC-LiNaK under MCFC standard reducing conditions.

Gas	H_2	CO_2	N_2	CO
Retention time (min)	1.3	3.5	5.2	7.2

2. Activation energy values calculated from Arrhenius plots within different temperature regions

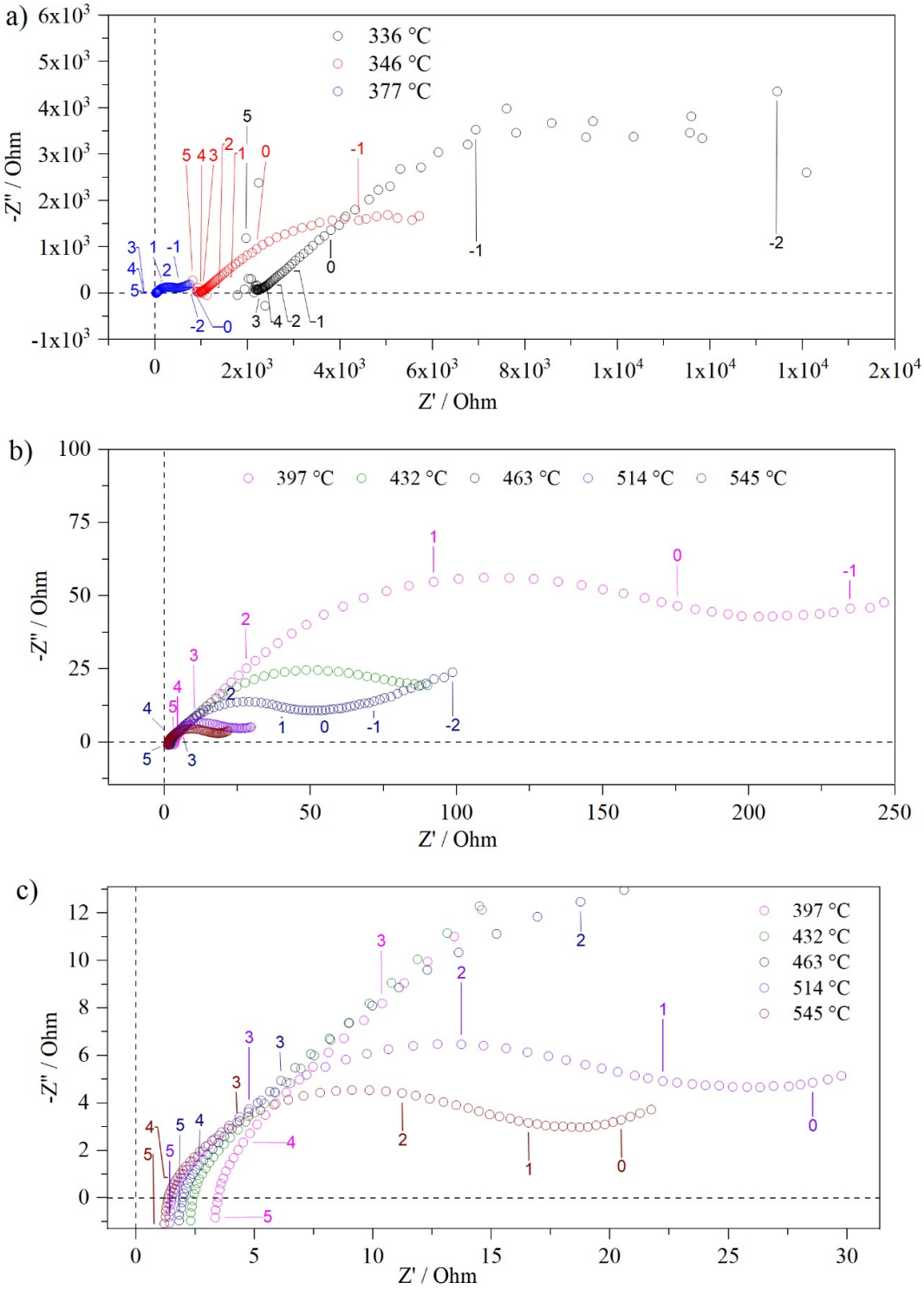

Figure S2. Nyquist EIS plots recorded in nitrogen atmosphere at different temperatures within the symmetric Au | SDC-LiNaK | Au electrochemical configuration. The amplitude of the applied sinusoidal voltage was V_0=100 mV. The numbers on the diagrams indicate the logarithm of the frequency of the applied signal.

Table S2. Activation energy (E_a) and transition temperature (t_t) values calculated from Arrhenius plot during thermal cycling of SDC-LiNaK under dry reducing atmospheres containing different amounts of hydrogen. H – heating; C – cooling; LT and HT – low and high temperature regions respectively.

Cycle	N_2 100 vol.%			Cycle	H_2 / N_2 : (23 / 77) vol.%		
	E_a, eV (LT)	E_a, eV (HT)	t_t, °C		E_a, eV (LT)	E_a, eV (HT)	t_t, °C
H1	2.08±0.06	0.27±0.02	367 395	H1	1.58±0.05	0.21±0.01	353 406
C1				C1	1.02±0.03	0.12±0.01	406
						0.49±0.02	361 315
						1.21±0.04	307
H2				H2	0.93±0.03	1.32±0.04	300 335
						0.17±0.01	397
C2				C2	0.73±0.02	0.14±0.01	407
						0.43±0.04	361 316
						1.53±0.07	307
Cycle	H_2 / N_2 : (50 / 50) vol.%			Cycle	H_2 100 vol.%		
	E_a, eV (LT)	E_a, eV (HT)	t_t, °C		E_a, eV (LT)	E_a, eV (HT)	t_t, °C
H1	1.63±0.03	0.21±0.01	357 397	H1	1.66±0.02	0.28±0.01	359 398
C1	0.81±0.02	0.13±0.01	406	C1	0.85±0.02	0.16±0.01	413
		0.39±0.02	397 310			0.42±0.02	345 308
		1.35±0.05	297			1.20±0.02	295
H2	0.84±0.01	1.43±0.05	305	H2	0.85±0.02	1.20±0.02	296
		0.24±0.01	324 386			0.31±0.02	310 366
		0.12±0.01	442			0.18±0.01	420
C2	0.75±0.03	0.13±0.01	394	C2	0.75±0.01	0.16±0.01	394
		0.41±0.01	362 309			0.45±0.02	318 305
		1.23±0.04	294			1.09±0.07	291

Table S3. Activation energy (E_a) and transition temperature (t_t) values calculated from Arrhenius plot during thermal cycling of SDC-LiNaK under oxidizing and reducing atmospheres both containing 20% of moisture. H – heating; C – cooling; LT and HT – low and high temperature regions respectively.

Cycle	N_2 / O_2 : (80 / 20) vol.% hum. 20%			Cycle	N_2 / H_2 : (77 / 33) vol.% hum. 20%		
	E_a, eV (LT)	E_a, eV (HT)	t_t, °C		E_a, eV (LT)	E_a, eV (HT)	t_t, °C
H1	1.62±0.02	0.24±0.01	353 396	H1	1.61±0.03	0.19±0.01	362 407
C1	1.95±0.07	0.22±0.01	403 369 314 286	C1	2.07±0.17	0.12±0.01	395 343 288 270
		0.55±0.22				0.37±0.01	
		1.39±0.03				1.10±0.02	
H2	1.75±0.06	1.60±0.02	295 325 392	H2	1.72±0.07	1.06±0.02	275 298 360 407
		0.22±0.01				0.27±0.01	
						0.14±0.01	
C2	2.13±0.12	0.24±0.02	407 379 302 279	C2	2.10±0.09	0.14±0.01	386 342 292 277
		0.55±0.02				0.39±0.01	
		1.71±0.03				1.06±0.01	

Table S4. Activation energy (E_a) and transition temperature (t_t) values calculated from Arrhenius plot during thermal cycling of SDC-LiNaK under MCFC standard oxidizing and reducing atmospheres. H – heating; C – cooling; LT and HT – low and high temperature regions respectively.

Cycle	N_2 / O_2 / CO_2 : (56 / 14 / 30) vol.%			Cycle	H_2 / CO_2 / H_2O : (64 / 16 / 20) vol.%		
	E_a, eV (LT)	E_a, eV (HT)	t_t, °C		E_a, eV (LT)	E_a, eV (HT)	t_t, °C
H1	1.65±0.05	0.31±0.01	354 407	H1	1.17±0.03	0.17±0.01	347 403
C1	1.97±0.03	0.33±0.01	396 352	C1	1.51±0.04	0.31±0.01	404 357
H2	1.95±0.03	0.26±0.01	356 407	H2	1.69±0.05	0.23±0.02	377 412
C2	2.05±0.03	0.27±0.02	400 344	C2	2.06±0.08	0.44±0.01	408 367

Reference

1. Meskine, H.; Gürbüz, E.; Albin, V.; Meléndez-Ceballos, A.; Cassir, M.; Ringuedé, A.; Lair, V. CO2 Electrolysis in a Reversible Molten Carbonate Fuel Cell: Online Chromatographic Detection of CO. *Int. J. Hydrogen Energy* **2021**, *46*, 14913–14921, doi:10.1016/J.IJHYDENE.2020.08.028.