Capture and electrochemical conversion of CO₂ to

value-added carbon and oxygen by molten salt electrolysis

Huayi Yin^a, Xuhui Mao^a, Diyong Tang^a, Wei Xiao^a, Luru Xing^a, Hua Zhu^a, Dihua Wang^{a,*}, Donald R Sadoway^b

Supporting Information

Reaction(500°C)	No.	$\Delta G(kJ / mol)$	$\Delta E(V)$
$Li_2CO_3 = Li_2O + C + O_2(g)$	(se1)	498.86	1.29
$Na_2CO_3 = Na_2O + C + O_2(g)$	(se2)	602.06	1.56
$K_2CO_3 = K_2O + C + O_2(g)$	(se3)	674.66	1.75
$Li_2CO_3 = 2Li + C + 1.5O_2(g)$	(se4)	995.62	1.72
$Na_2CO_3=2Na+C+1.5O_2(g) \\$	(se5)	900.48	1.56
$2K_2CO_3 = 4K + 2C + O_2(g)$	(se6)	913.54	1.58
$CO_2(g) = C + O_2(g)$	(se7)	395.5	1.02
$Na_2O = 2Na + O_2(g)$	(se8)	623.89	1.62
$K_2O = 2K + O_2(g)$	(se9)	505.47	1.31
$Li_2O = 2Li + O_2(g)$	(se10)	993.50	2.57
$Na_2O + Li_2CO_3 = Na_2CO_3 + Li_2O$	(se11)	-103.2	
$K_2O + Li_2CO_3 = K_2CO_3 + Li_2O$	(se12)	-175.8	
$Li_2O + CO_2 (g) = Li_2CO_3$	(se13)	-103.34	

Table S1 Thermodynamics data and dissociation potential of typical reactions (data from HSC 5.0)

Table S2 BET surface area of the carbon obtained under different cell voltages

Carbon powder prepared at different voltages	2.8V	3.0V	3.5V	4.0V	4.5V	5.0V
BET $(m^2 g^{-1})$	414	562	497	449	616	558

Elements	Content (wt%)	Elements	Content (wt%)
С	86.39	Cr	0.0071
0	12.7	Fe	0.149
Na	0.041	Ni	0.0258
Mg	0.012	Cu	0.0266
S	0.0148	Zn	0.00939
Cl	0.264	Zr	0.00094
Κ	0.167	Ag	0.0968
Ca	0.062	Sn	0.0067
Ti	0.0046		

Table S3 Composition of the deposited carbon material on Ni cathode (XRF measurement)*

*: Elements except for C and O in the table were calculated as impurity.



Figure S1 CVs of Ni electrode in Na₂CO₃-K₂CO₃ melt at 750 °C (a) and Li₂CO₃-Na₂CO₃-K₂CO₃

melt at 500° C (b)



Figure S2 Equilibrium constant (K) of the reaction $(CO_2(g) + Li_2O = Li_2CO_3)$ at different temperatures. Data were obtained by the standard $\triangle G$ data in HSC Chemistry 5.0.



Figure S3 TEM images of the carbon obtained at 2.8V (a) and 4.0V (b)



Figure S4 (a) CVs of the carbon film electrode in 1M H_2SO_4 solution; (b) Nyquist plot of the carbon film electrode at open circuit (10mHz-100kHz, $\pm 5mV$). Carbon powders used for preparation of the film electrode were obtained at 4V.



Figure S5 Digital photos of Ni, Fe and Cu anodes before and after CV scan



Figure S6 XRD patterns of the corrosion products of Cu anode and Ni anode used in the Li₂CO₃-Na₂CO₃-K₂CO₃ eutectic molten

Supplementary experimental information:

1) GC analytical condition

The composition of the effluent gas (before and during electrolysis) was analyzed using an online GC. The GC instrument can automatically sample the effluent gas at a certain frequency through an online sampler. Standard gas (5.18 mol% O_2 , 10.27 mol %, 9.91 mol% CO and 10.33mol% CO_2 in Argon) was used for building calibration line for quantitative analysis.

Carrier gas: High purity Argon gas (0.15 MPa at inlet)

Temperature of injection valve: 110 °C

Temperature of analytic column: 80 °C

Temperature of TCD detector: 110 °C

Running time: 20 min/sample

2) Procedure of calcination experiment for carbon

Alumina crucible was calcinated at 1000 °C for two hours and was weighed. 2) Around 100 mg prepared carbon was transferred into the crucible and was calcinated at 800 °C for 2 hours. 3)The crucible was weighed and the calcination loss of the carbon powder (or residual ash) was calculated.