Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information

An Oxygen Pumping Anode for Electrowinning Aluminium

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Figure 1: XRD of the $LaMnO_3$ powder

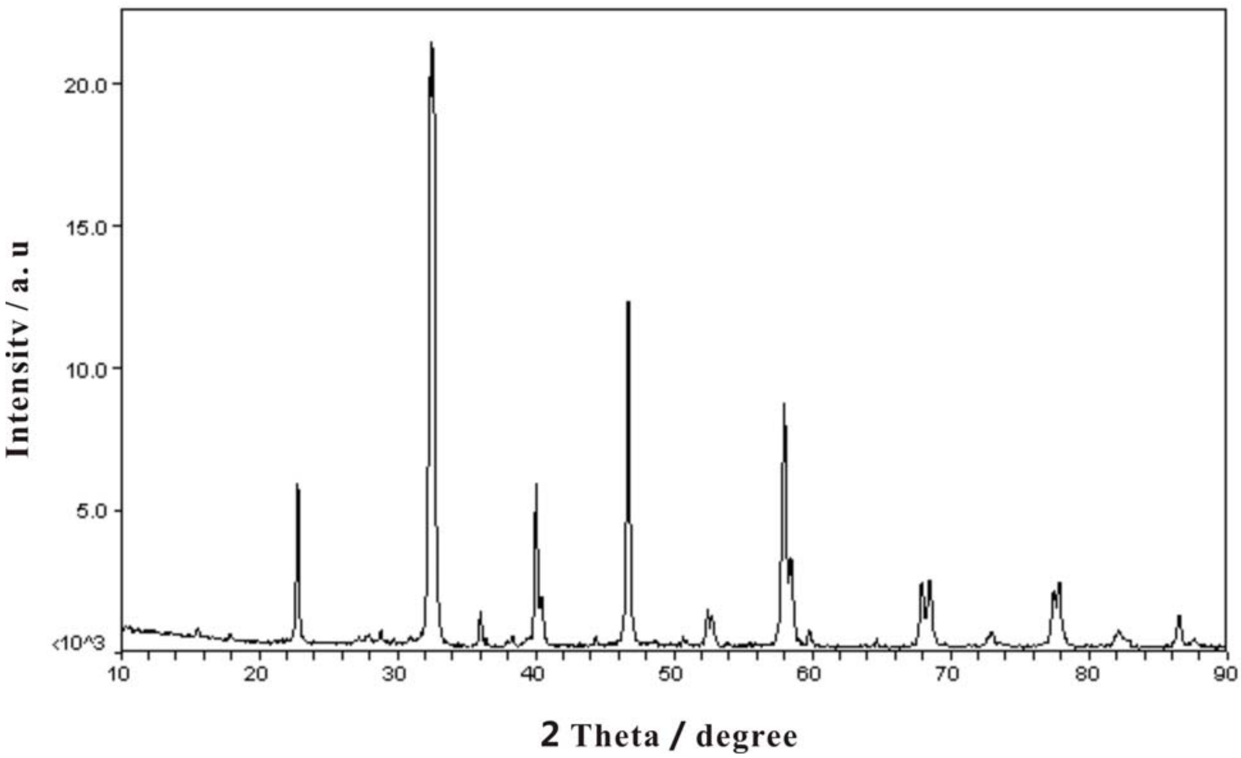


Figure 2: Diagram of the oxygen pumping anode (a) and the photograph of YSZ tube (b).

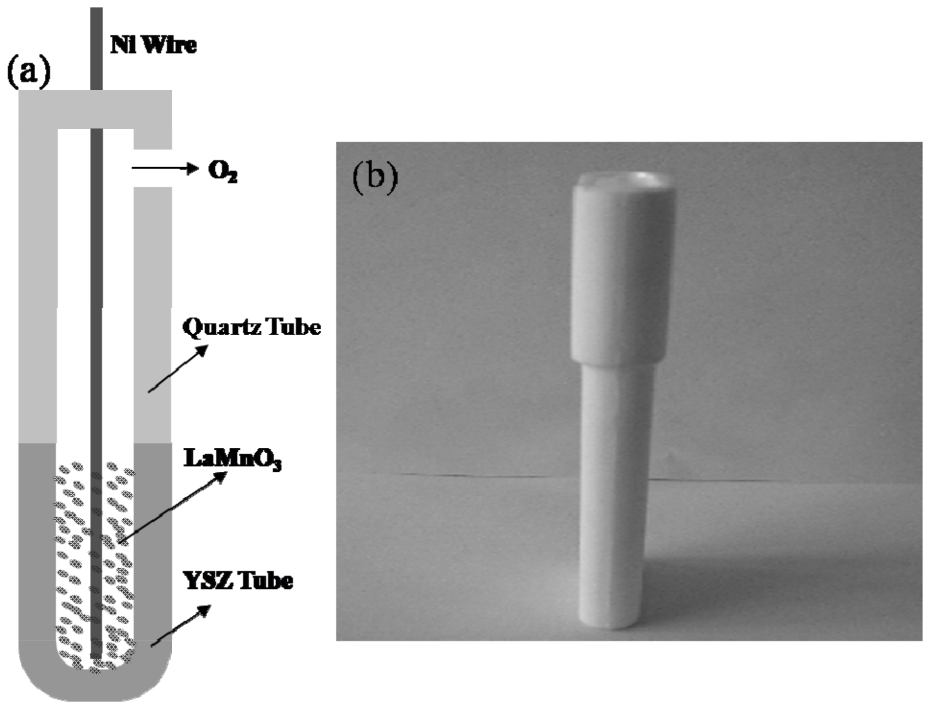
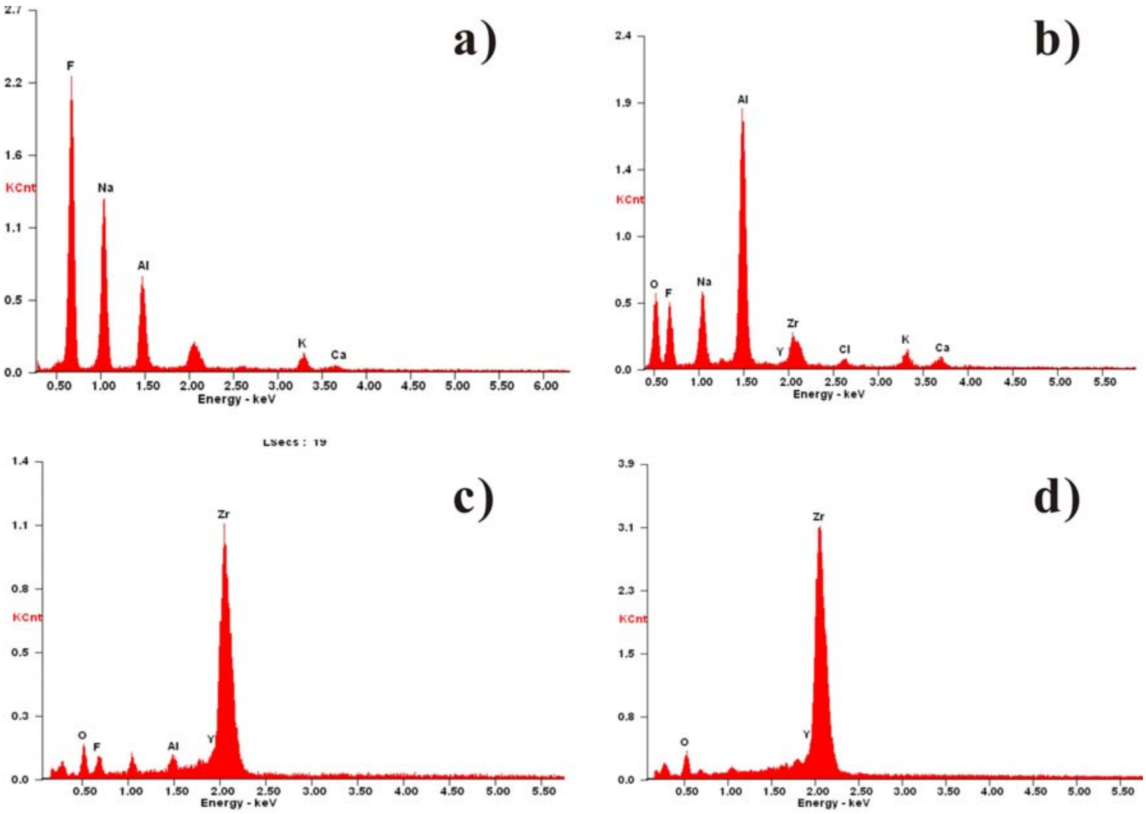


Figure 3: EDX analysis of red spots in SEM images: (a) top layer (b) 17 μm (c) 65 μm (d) 70 μm



Calculation of the free energy of chemical reaction:

Table S1: All the potential chemical reactions in the electrolysis cell

$3ZrO_2 + 4\,Na_3AlF_6 = 3ZrF_4 + 2\,Al_2O_3 + 12NaF$	$Y_2O_3 + 2\,Na_3AlF_6 = 2YF_3 + Al_2O_3 + 6NaF$
$3ZrO_2 + 4\,AlF_3 = 3ZrF_4 + 2\,Al_2O_3$	$Y_2O_3 + 2\,AlF_3 = 2YF_3 + Al_2O_3$
$ZrO_2 + 2\,MgF_2 = ZrF_4 + 2\,MgO$	$Y_2O_3 + 3MgF_2 = 2YF_3 + 3MgO$
$ZrO_2 + 2\,CaF_2 = ZrF_4 + 2\,CaO$	$Y_2O_3 + 3CaF_2 = 2YF_3 + 3CaO$
$ZrO_2 + 4LiF = ZrF_4 + 2\,Li_2O$	$Y_2O_3 + 6LiF = 2YF_3 + 3Li_2O$
$3ZrO_2 + 4Al = 3Zr + 2\,Al_2O_3$	$Y_2O_3 + 2Al = 2Y + Al_2O_3$
$ZrO_2 + 2C = Zr + 2CO$	$Y_2O_3 + 3C = 2Y + 3CO$
$ZrO_2 + 4NaF = ZrF_4 + 2Na_2O$	$Y_2O_3 + 6NaF = 2YF_3 + 3Na_2O$

Table S2: The standard enthalpy of formation at 298 K and Gibbs free energy function at 1200K

Chemcials	$-\Delta_f H^{\Theta}_{m,298}$ /J·mol^{-1}	$\phi_T^{'}$ /J·mol^{-1}·K^{-1}
ZrO_2	1097463	93.065
Y_2O_3	1905394	173.925
Na_3AlF_6	3309544	403.326
ZrF_4	1911251	183.918
Al_2O_3	1675274	117.084
NaF	573626	83.83
MgF_2	1123404	103.311
LiF	616931	68.851
MgO	601241	55.77
CaF_2	634294	70.894
GaO	634294	70.894
C	0	14.99
Al	0	48.382
Zr	0	57.123
Y	0	62.442
CO	110541	216.99
Li_2O	166942	264.650
ZrF_4	1911251	183.918
YF_3	1718369	174.083

Table S3: The calculated free energy at 1200K

Reactions	ΔG_T^Θ /kJ·mol^{-1}
$Y_2O_3 + 2Na_3AlF_6 = 2YF_3 + Al_2O_3 + 6NaF$	-14.500
$Y_2O_3 + 2AlF_3 = 2YF_3 + Al_2O_3$	-181.909
$Y_2O_3 + 3MgF_2 = 2YF_3 + 3MgO$	-3401.600
$ZrO_2 + \frac{4}{3}NaAlF_6 = ZrF_4 + \frac{2}{3}Al_2O_3 + 4NaF$	-3105.500

Table S4: Element analysis of (a) top layer

Element	F*K*	Na*K*	Al*K*	K*K*	Ca*K*
Wt%	42.76	35.53	17.87	3.09	0.76
At%	49.04	33.92	14.53	1.73	0.42

Table S5: Element analysis of (b) 17 μm

Element	O*K*	F*K*	Na*K*	Al*K*	Y*L*	Zr*L*	Cl*K*	K*K*	Ca*K*
Wt%	20.53	18.74	12.84	30.97	0.65	10.27	1.24	2.88	1.88
At%	30.19	23.20	13.14	27.00	0.17	2.65	0.82	1.73	1.10

Table S6: Element analysis of (c) 65μm

Element	O*K*	F*K*	Al*K*	Y*L*	Zr*L*
Wt%	16.39	9.49	1.47	5.44	67.21
At%	43.11	21.01	2.29	2.58	31.01

Table S7: Element analysis of (d) 70 μm

Element	O*K*	Y*L*	Zr*L*
Wt%	16.33	5.64	78.03
At%	52.63	3.27	44.10