New Journal of Chemistry

Supplementary Information

Perovskite Chromate Doped with Titanium for Direct Carbon Dioxide Electrolysis

Weitang Yao,[+a,b] Tao Duan,[+a] Yuanxin Li,[+b] Liming Yang,[b] Kui Xie*[a,b]

[a]National School of Defense Technology, Laboratory of Extreme Conditions Matter Properties, Southwest University of Science and Technology, Mianyang, Sichuan 621000, P. R. China

[b]Key Laboratory of Advanced Functional Materials and Devices, School of Materials Science and Engineering, Hefei University of Technology, No.193 Tunxi Road, Hefei, Anhui 230009, China

*Corresponding: xiekui@hfut.edu.cn

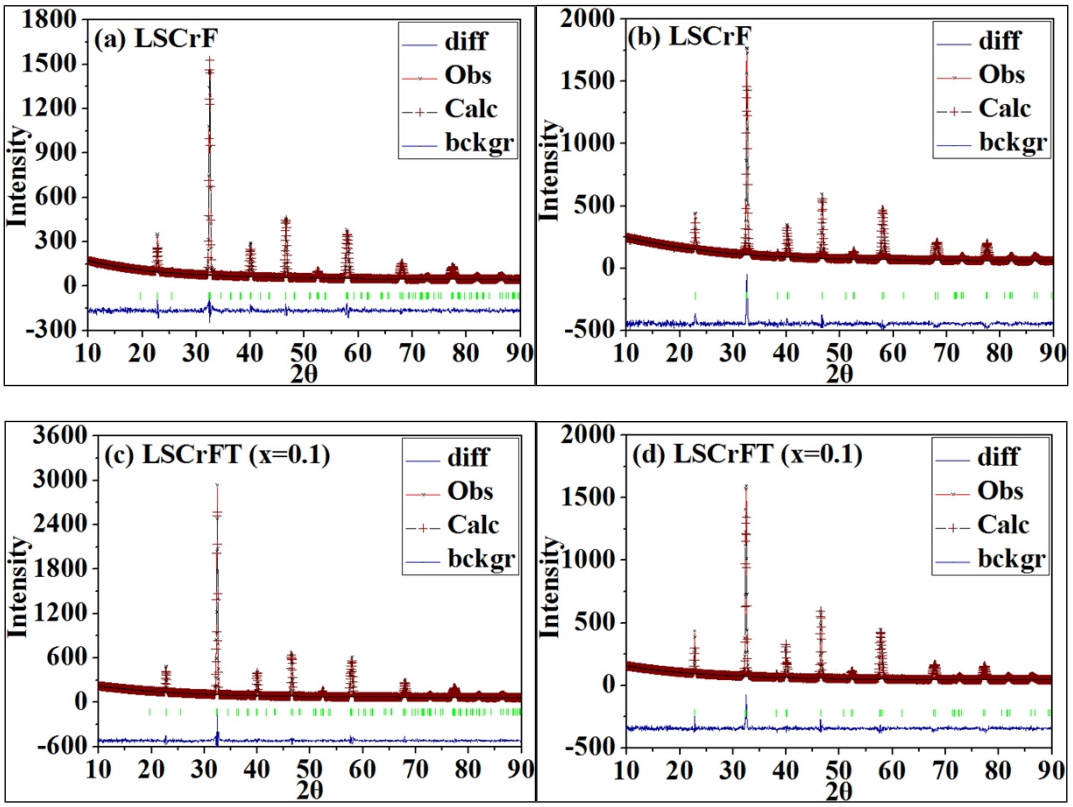

Figure S1. Rietveld refinement results for LSCrF and LSCrFT (x=0.1): (a), (c)

oxidized powders synthesized in air at 1400 °C for 10 h; (b), (d) reduced powders prepared at 800 °C in 5%H_2/Ar for 5 h.

Figures S1a and c show the XRD patterns of LSCrF and LSCrFT (x=0.1) which are refined with GSAS software indicating a perovskite structure with space group of *Pnma* for oxidized samples. The refinement results are shown in Table S1 and Table S2. It shows the expansion of the cell parameters of a, b and c with the increasing contents of Ti for the oxidized LSCrFT. Figures S1b and d show space group of *R-3c* for the reduced samples. The reduced LSCrFT show a similar expansion for the cell parameters. The different valence states and radiuses of Ti (+4) and Cr (+3, +6) in the lattice may have influence on the unit cell parameters.

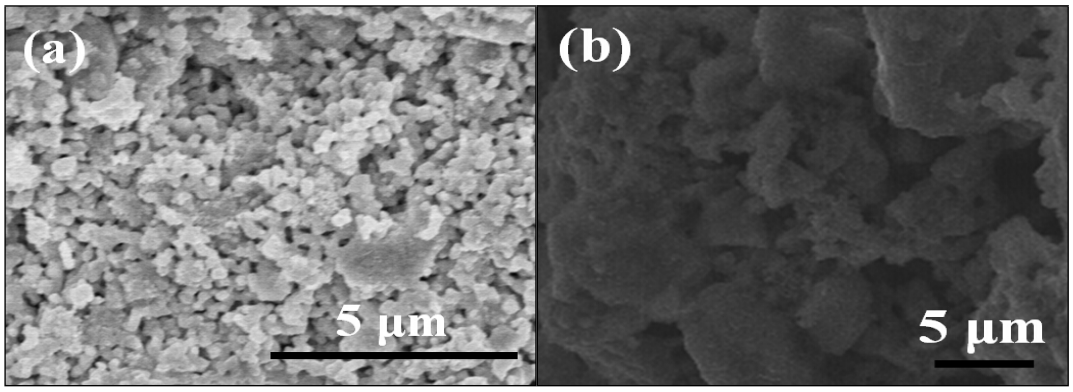

Figure S2. FESEM images for cathodes based on (a) LSCrF-YSZ and (b) LSCrFT(x=0.1)-YSZ after carbon dioxide electrolysis tests at 800 °C.

Figure S2 shows the microstructures of the cathodes based on LSCrF-YSZ and LSCrFT(x=0.1)-YSZ after carbon dioxide electrolysis at 800 °C. The composite electrodes are porous and the particle size is generally uniform. Table S3 shows the different binding energies of the elements in LSCrF and LSCrFT (x=0.1) powders.

Table S4 presents $Cr^{3,\ 4+}/Cr^{6+}$ of 74.2:25.8 for LSCrF and 74.3:25.7 for LSCrFT (x=0.1). The ratio of Fe^{3+}/Fe^{4+} is a little different for the two kinds of ceramics. The oxidized LSCrFT shows a little higher percentage of Fe^{3+} than LSCrF in order to keep valence state balance which may be due to the doped Ti with main chemical state +4. In reduced LSCrF and LSCrFT (x=0.1), both the samples show main chemical state of +3 for Cr and Fe. The percentage of Ti^{3+} in Ti is ~12.5% for the reduced LSCrFT (x=0.1).

x	a(Å)	b(Å)	c(Å)	Rwp (%)	Rp (%)	Chi^2
0	5.4935(4)	7.7897(4)	5.52609(32)	10.92	8.27	1.000
0.1	5.50509(20)	7.78249(29)	5.54192(21)	9.96	7.72	1.149
0.2	5.51738(22)	7.80220(27)	5.54743(18)	10.20	7.81	1.032
0.3	5.52806(25)	7.81449(33)	5.55205(24)	8.14	6.28	1.085
0.4	5.5398(4)	7.8318(5)	5.5407(4)	10.48	8.07	1.165
0.5	5.5367(24)	7.82203(32)	5.55877(26)	7.75	6.00	1.021

Table S1 Unit cell parameters and Rietveld refinement results for the oxidized $La_{0.75}Sr_{0.25}Cr_{0.5-x}Fe_{0.5}Ti_xO_{3-\delta}$ with the space group *Pnma*.

x	a(Å)	b(Å)	c(Å)	Rwp (%)	Rp (%)	Chi^2
0	5.52550(24)	5.5255	13.4508(10)	10.48	8.23	1.279
0.1	5.53286(13)	5.53286	13.4624(6)	11.63	9.16	1.110
0.2	5.53732(23)	5.53732	13.5190(10)	9.86	7.63	1.216
0.3	5.53387(15)	5.53387	13.5868(7)	8.94	6.97	1.140
0.4	5.55750(26)	5.5575	13.6508(12)	10.27	7.95	1.286
0.5	5.56959(28)	5.56959	13.6390(14)	8.17	6.83	1.187

Table S2 Unit cell parameters and Rietveld refinement results for the reduced $La_{0.75}Sr_{0.25}Cr_{0.5-x}Fe_{0.5}Ti_xO_{3-\delta}$ with the space group *R-3c*.

Element	Cr		Fe		Ti	
	Cr^{3+}	Cr^{6+}	Fe^{3+}	Fe^{4+}	Ti^{3+}	Ti^{4+}
$2p_{1/2}$ (eV)	585.8	587.9	723.4	724.9	463.4	464.0
$2p_{3/2}$ (eV)	576.2	578.7	710.5	714.1	458.2	458.5

Table S3 Binding energies for Cr, Fe and Ti elements in LSCrF and LSCrFT (x=0.1) according to the XPS results.

	Oxidized state			Reduced state		
	$Cr^{3,4+}/Cr^{6+}$	Fe^{3+}/Fe^{4+}	Ti	Main chemical state		Ti^{3+}/Ti^{4+}
LSCrF	74.2:25.8	82.9:17.1	-	Cr^{3+}	Fe^{3+}	-
LSCrFT(x=0.1)	74.3:25.7	84.1:15.9	Ti^{4+}	Cr^{3+}	Fe^{3+}	12.5:87.5

Table S4 Percentages for different valence states of Cr, Fe and Ti in LSCrF and LSCrFT (x=0.1) according to the XPS results.