

Supporting Information

Electrocatalytic water oxidation at low energy cost by a highly active and robust calcium-manganese oxide thin film sintered on FTO electrode with ethylmethyl imidazolium triflate ionic liquid.

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Materials. The FTO conducting glass sheet (fluorine doped SnO₂, sheet resistance: 7 Ω/sq., transmission, 90% in the visible region) was obtained from SPD Laboratory, Inc. MnCl₂·4H₂O (99.0 %) was purchased from Chameleon Co. CaCl₂ was purchased from Nacalai Tesque, Inc. 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMI triflate), KH₂PO₄ (≥ 99%), K₂HPO₄ (≥ 99%), KOH, NaOH (≥ 86%), HClO₄, and NaClO₄ (99.99%,) were purchased from Sigma-Aldrich Co. All reagents were used as received without further purification. Mill-Q water (18 M Ω.cm) was used for buffer solutions preparation.

Instruments and characterization. The electrochemical measurements were carried out on an Autolab Potentiostat/Galvanostat model PGSTAT128N. Particle morphologies and sizes were observed by scanning electron microscopy, Field Emission Hitachi Model S-4300 scanning electron microscope operated at 15 KV accelerating voltage and 15 mm working distance. The X-ray diffraction patterns (XRD) were collected by Rigaku Co. XRD patterns were recorded from 15° to 90° in 2θ at a step size of 0.05° and a scan rate of 0.25°/min. Gas chromatographic analyses were done with a Shimadzu GC-8A equipped with a capillary column (0.53 mm ID x 15 m) with a Molecular Sieve 5A layer at 40 °C using Ar as a carrier gas. XP spectra were obtained using a Ulvac Phi 5000 VersaProbe CU X-ray Photoelectron Spectrometer with a Multipak data treatment system. The photoelectrons emitted by a monochromated Al Kα (1486.6 eV; 350 W) radiation were collected with path energy of 23.5 eV through a hemispherical analyzer. The pressure in the analyzing chamber was below 1 x 10⁻⁹ Torr during the measurements. All spectra in XPS were calibrated to C 1s = 284.6 eV.

Preparation of α-Mn₂O₃ and CaMn-Oxide EMI triflate-containing precursor solutions. The EMI triflate containing precursor solution of α-Mn₂O₃ was prepared by dissolving MnCl₂·4H₂O (1.0 g, 5.05 mmol) in MeOH (4 mL). The solution was then sonicated for ~ 1 h. EMI triflate solution (1.0 mL) was then added to the

solution and the mixture was further sonicated for ~ 1 h. The EMI triflate-containing precursor solution of CaMn-Oxide was prepared similarly by dissolving a mixture of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (1.0 g, 5.05 mmol) and CaCl_2 (0.56 g, 5.05 mmol) in MeOH (4 mL) and EMI triflate (1 mL).

Preparation of FTO/EMI $\alpha\text{-Mn}_2\text{O}_3$ and FTO EMI CaMn-Oxide electrodes.

FTO sheet was cut down to rectangular plates of 5.0 cm x 3.0 cm, sonicated in de-ionized water and acetone for 15 min each, and then dried in an oven at 60 °C. An adhesive NITOFLO[®] tape No. 973UL (Nitto Denko Co., Ltd) was attached on the plate (2 layers of tape) in such a way that 1.0 cm x 5.0 cm of the plate remained uncovered. The EMI triflate containing precursor solution of $\alpha\text{-Mn}_2\text{O}_3$ or CaMn-Oxide (200 μL) was spread over the uncovered 1.0 cm x 5.0 cm of the plate then justified with a glass tube using a doctor Blading technique at 110 °C. The tape was then removed, and the electrodes containing the precursor films were sintered in an oven at 550 °C for 1 h under air. After cooling down, the electrodes was washed strongly with tap water to leave a strongly attached layer of $\alpha\text{-Mn}_2\text{O}_3$ and CaMn-Oxide on the FTO electrodes called FTO/EMI $\alpha\text{-Mn}_2\text{O}_3$ and FTO/EMI CaMn-Oxide. The electrodes were then cut into suitable pieces (1.0 cm x 3.0 cm) for the characterization and measurements.

Electrochemical measurements. The electrochemical measurements were performed under an argon atmosphere using a conventional three-electrode cell. The working electrode was FTO/EMI $\alpha\text{-Mn}_2\text{O}_3$ or FTO/EMI CaMn-Oxide. A Pt wire and a Ag/AgCl (3 M NaCl) were the counter and reference electrodes, respectively. While all measurements were carried out using a Ag/AgCl (3 M KCl) reference electrode, the results in this study are presented against the normal hydrogen electrode (NHE) by addition of 0.198 V to the potential measured with respect to Ag/AgCl (3 M NaCl) reference electrode. All measurements were made in a 0.1 M potassium phosphate buffer (pH 7.0) or 1 M NaOH solutions at 25°C.

Bulk electrolysis and oxygen measurements. Bulk electrolysis was performed in a two compartment gas-tight electrochemical cell with a glass frit junction of fine porosity. The cell was filled with 0.1 M KPi (pH 7.0) or 1 M NaOH solutions. The solution was degassed by Ar for 20 min. The FTO/EMI $\alpha\text{-Mn}_2\text{O}_3$ or FTO/EMI CaMn-Oxide and Ag/AgCl (3 M NaCl) working and reference electrodes were inserted close to each other and a Pt foil (20 cm²) was used as a counter electrode. The evolved O₂

in the working electrode compartment was measured as previously reported using gas chromatography.¹

Table S1. Atomic composition ratio of the FTO/EMI α -Mn₂O₃ and FTO/EMI CaMn-Oxide electro-catalysts measured by XPS.

Electro-catalyst	C	N	O	F	S	Ca	Mn	Formula
FTO/EMI α -Mn ₂ O ₃	0.30	0.03	0.48	0	0.004	0	0.19	α -Mn ₂ O ₃ .2H ₂ O
FTO/EMI CaMn-Oxide	0.38	0.06	0.33	0.05	0.021	0.073	0.082	Ca _{0.89} Mn-Oxide

Table S2. XPS deconvoluted values of C 1s, N 1s, O 1s, F 1s, S 2p, Ca 2p, Mn 2p_{3/2}, Mn 2p_{1/2}, and Mn 3s for FTO/EMI α -Mn₂O₃ and FTO/EMI CaMn-Oxide electro-catalysts.

	FTO/EMI α-Mn₂O₃	FTO/EMI CaMn-Oxide
C 1s	283.4	282.73
	284.8	284.86
	285.58	285.27
	286.44	286.82
	288.02	288.26
N 1s	400.18	400.41
O 1s	529.57	529.4
	530.97	529.52
	532.83	531.59
		532.83
		533.71
F 1s		685.85
		686.69
S 2p		170.08
Ca 2p		345.75
		349.31
		352.07
		353.19
Mn 2p _{3/2}	640.98	640.56
	642.64	641.83
		643.73
Mn 2p _{1/2}	652.61	651.52
	653.49	652.94
		654.29
Mn 3s	83.18	83.15
	88.83	88.63
ΔE Mn 3s	5.65	5.48
Mn Valencies	II, III	II, III, IV

Table S3. Simulated R_s , R_{ct} , and CPE of FTO/EMI CaMn-Oxide and FTO/EMI α - Mn_2O_3 electro-catalysts obtained from the Electrochemical impedance spectroscopy (EIS) measurements performed at different applied potentials.

$E_{app}(V)$	FTO/EMI CaMn-Oxide			FTO/EMI α - Mn_2O_3		
	R_s (Ω/cm^2)	R_{ct} (Ω/cm^2)	CPE	R_s (Ω/cm^2)	R_{ct} (Ω/cm^2)	CPE
0.198	95.6	4,773.4	1.7×10^{-4}	276.7	21, 147	5.9×10^{-5}
0.998	41.6	24,544	6.5×10^{-5}	2,154.4	21, 725	7.3×10^{-5}
1.098	46.4	14, 587	1.1×10^{-4}	1,008.6	1,531.8	1.4×10^{-6}
1.198	69.7	1,747	1.7×10^{-4}	2182.5	15,959	9.9×10^{-5}
1.298	69.7	1,747	1.7×10^{-4}	2,069.1	7,915.7	2.0×10^{-4}
1.298	94.5	212.3	1.2×10^{-4}	907.1	1,455.8	9.8×10^{-7}
1.389	62.3	71.4	9.3×10^{-5}	49.2	368.3	9.6×10^{-7}

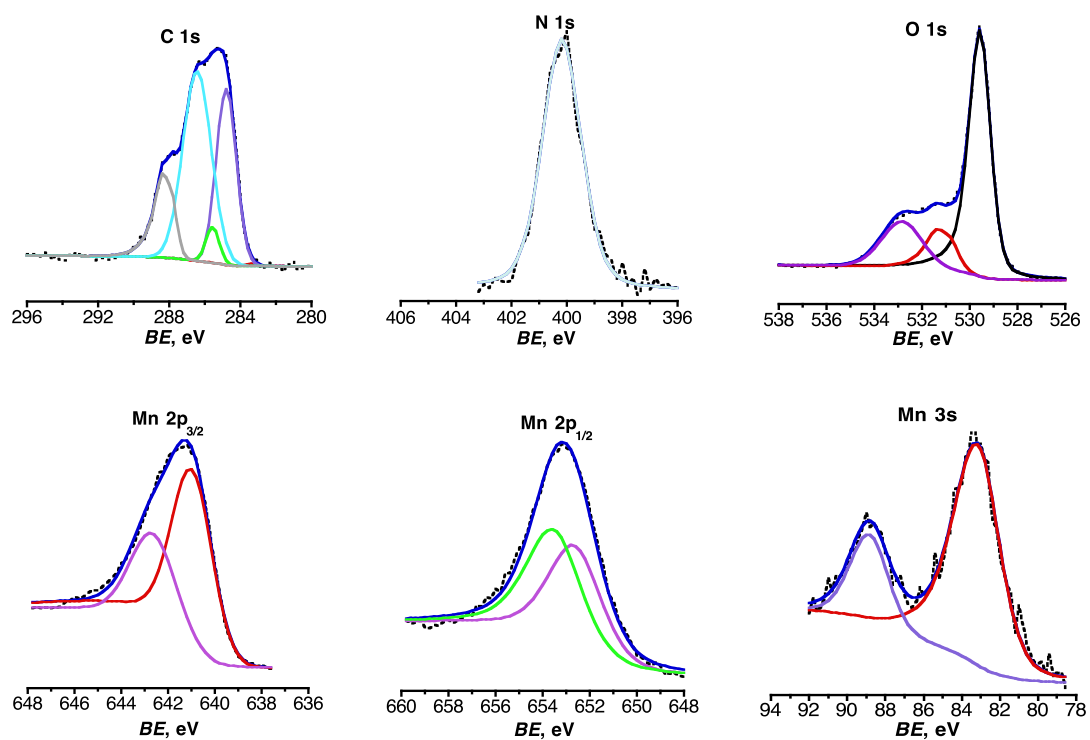


Figure S1. XPS deconvolution of C 1s, N 1s, O 1s, Mn 2p_{3/2}, Mn 2p_{1/2}, and Mn 3s of the FTO/EMI α -Mn₂O₃ electro-catalyst.

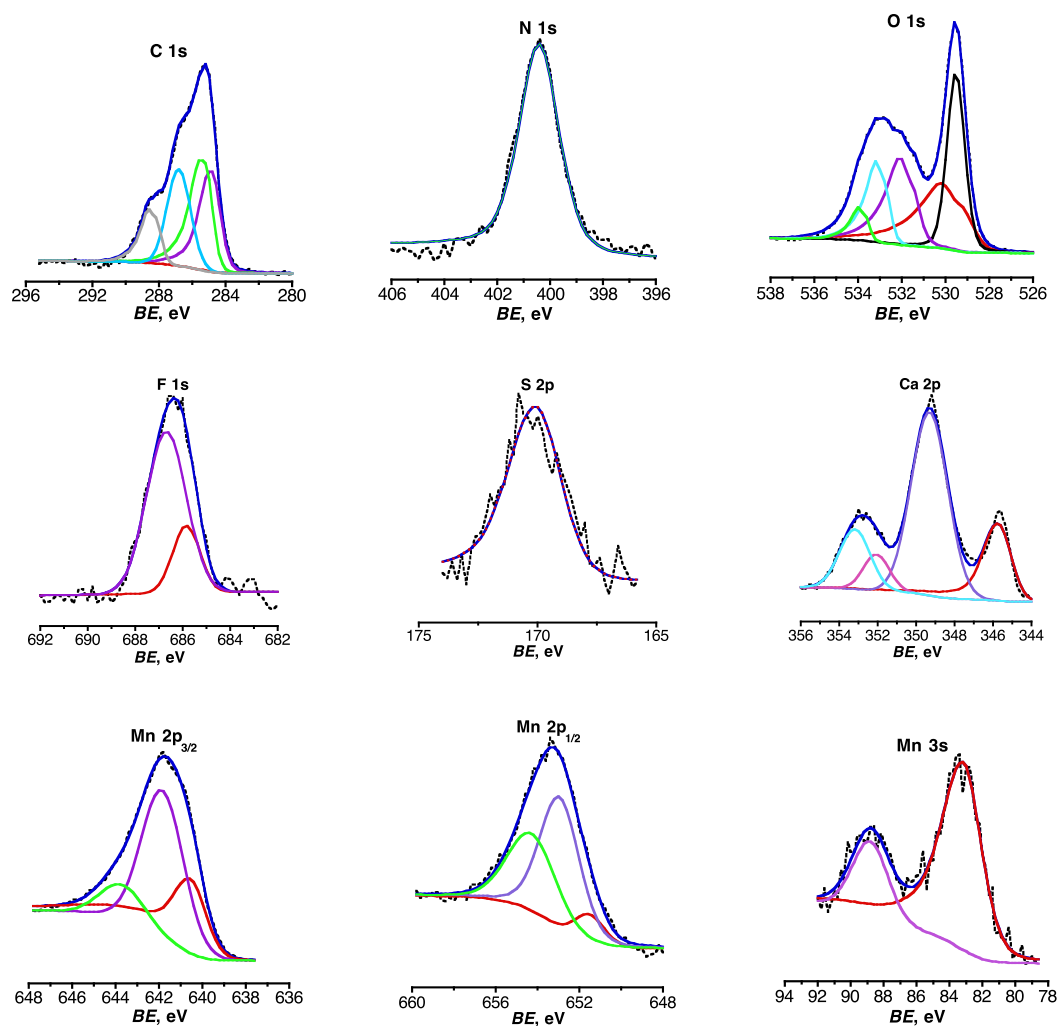


Figure S2. XPS deconvolution of C 1s, N 1s, O 1s, F 1s, S 2p, Ca 2p, Mn 2p_{3/2}, Mn 2p_{1/2}, and Mn 3s of the FTO/EMI CaMn-Oxide electro-catalyst.

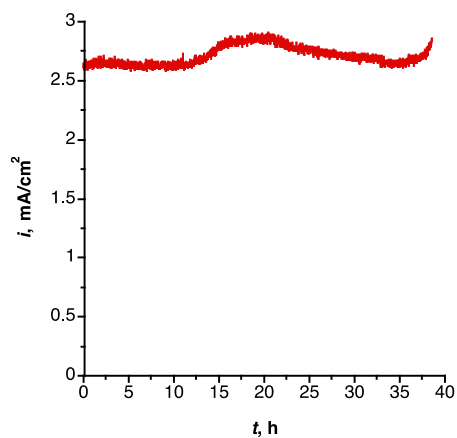


Figure S3. Current-time profile of a bulk electrolysis conducted at 1.38 V applied potential of FTO/EMI CaMn-Oxide electro-catalyst in a 0.1 M KP_i buffer solution (pH 7.0).

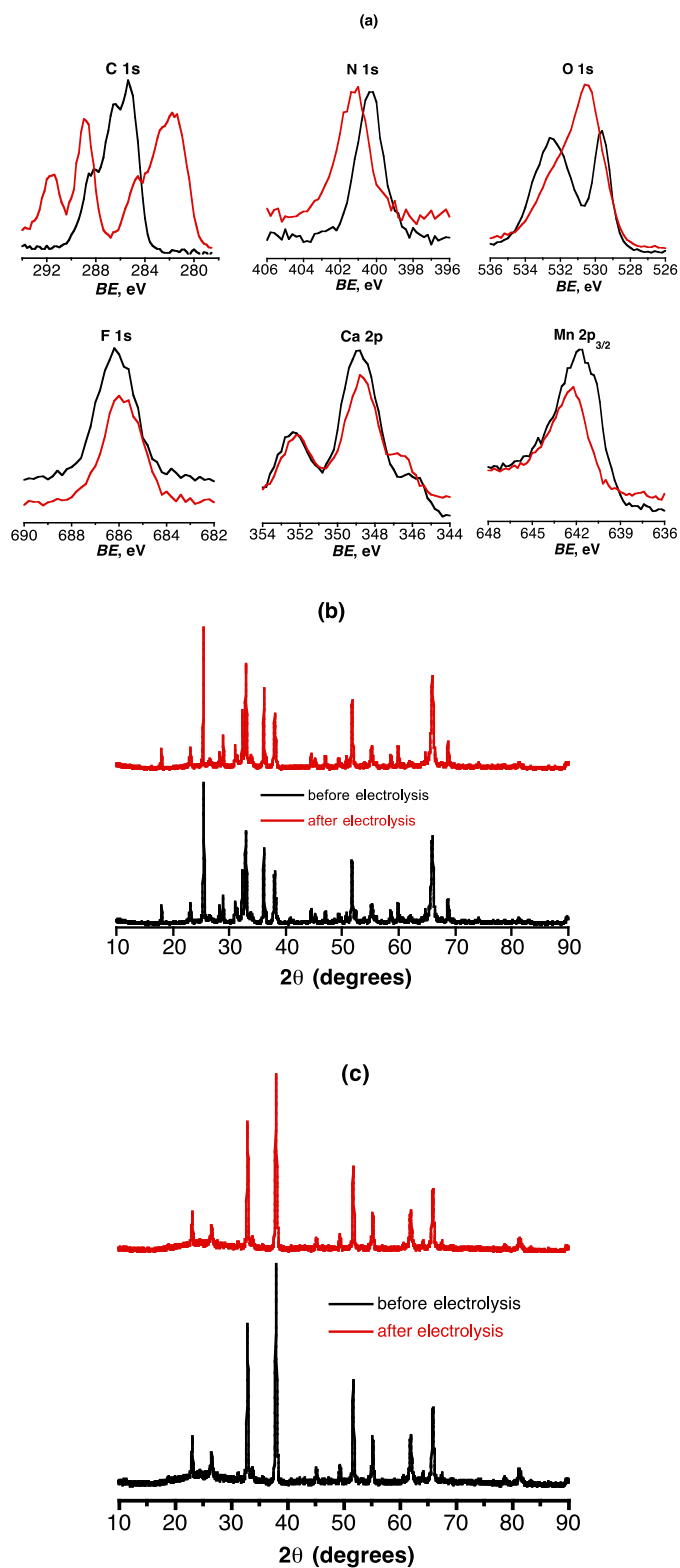


Figure S4. (a) XP spectra of C 1s, N 1s, O 1s, F 1s, Ca 2p, and Mn 2p_{3/2} of FTO/EMI CaMn-Oxide electro-catalyst before (black lines) and after (red lines) electrolysis at 1.39 V for 40 h. (b) XRD patterns before and after electrolysis of FTO/EMI CaMn-Oxide. (c) XRD patterns before and after electrolysis of FTO/EMI α -Mn₂O₃.

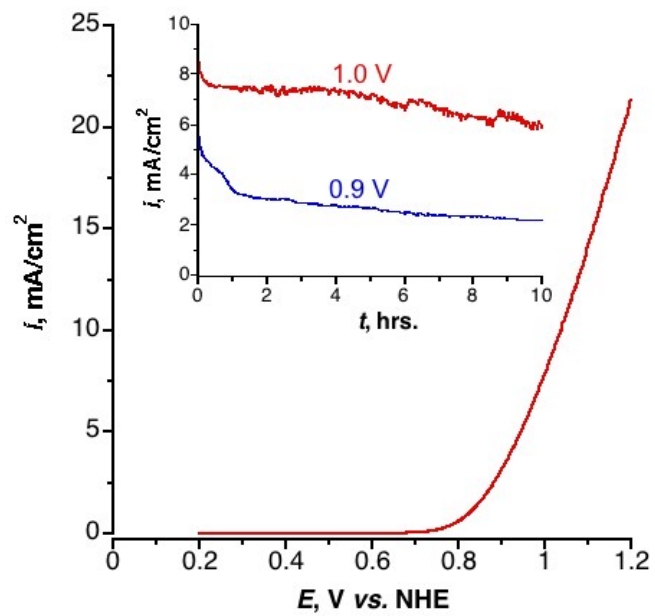


Figure S5. LSV at 5 mV/s scan rate of FTO/EMI CaMn-Oxide in 1 M NaOH. Inset: controlled potential electrolysis at 0.9 and 1.0 V in 1M NaOH.

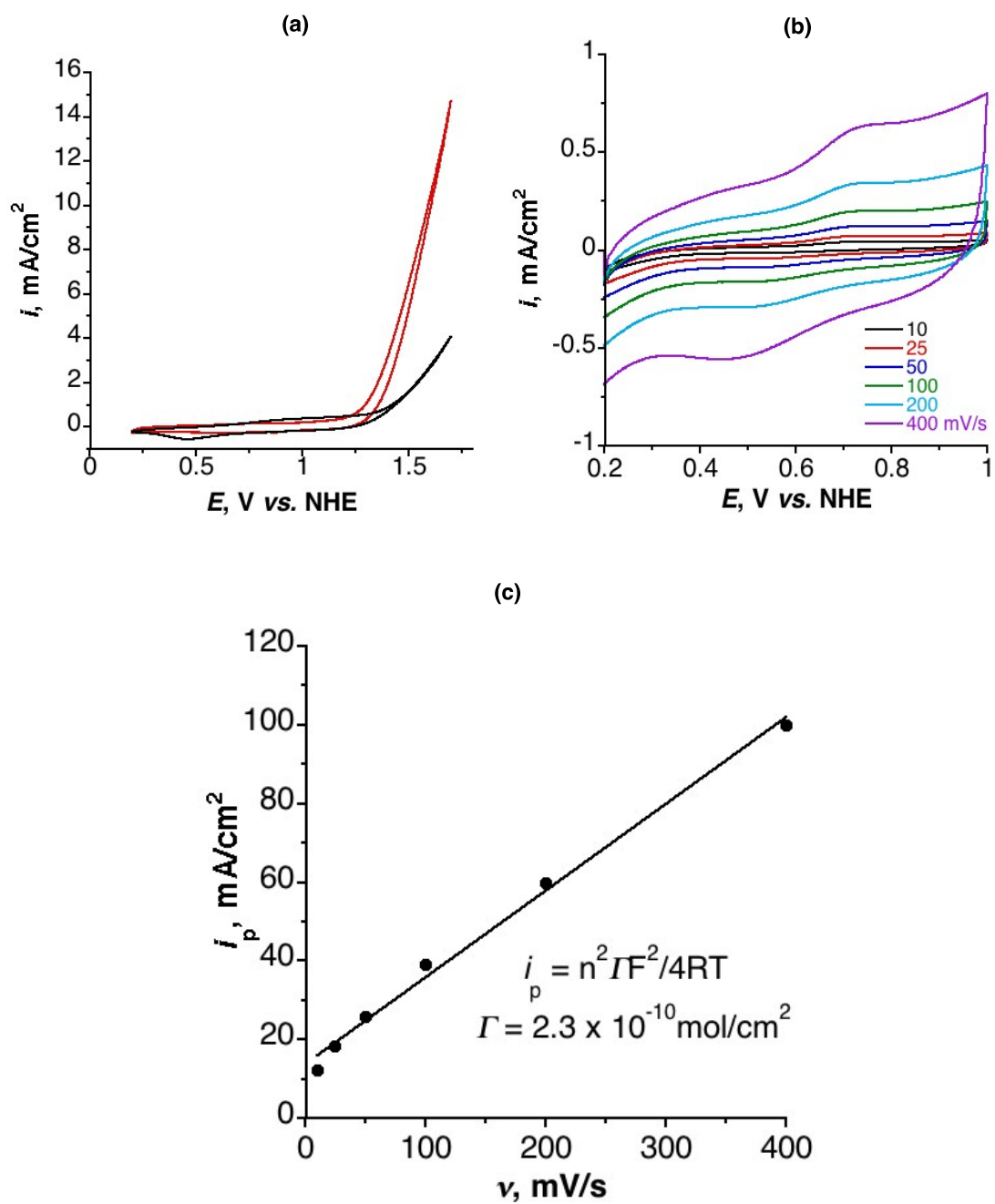


Figure S6. (a) CVs at 50 mV/s scan rate of FTO/EMI α -Mn₂O₃ (black line) and FTO/EMI CaMn-Oxide (red line) in a 0.1 M KPi buffer solution (pH 7.0). (b) CVs at different scan rates of FTO/EMI CaMn-Oxide. (c) Current density-scan rates relationship derived from (b).

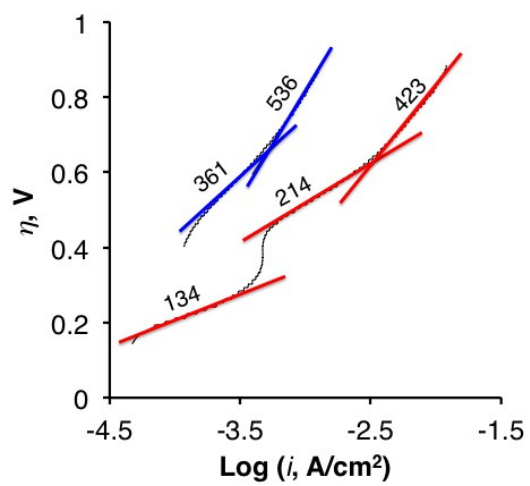


Figure S7. Tafel plots and Tafel slope values of FTO/EMI CaMn-Oxide (red lines) and FTO/ α - Mn_2O_3 (blue lines) measured in a 0.1 M KPi buffer solution (pH 7.0) without iR correction. Values are Tafel slopes in mV/decade.

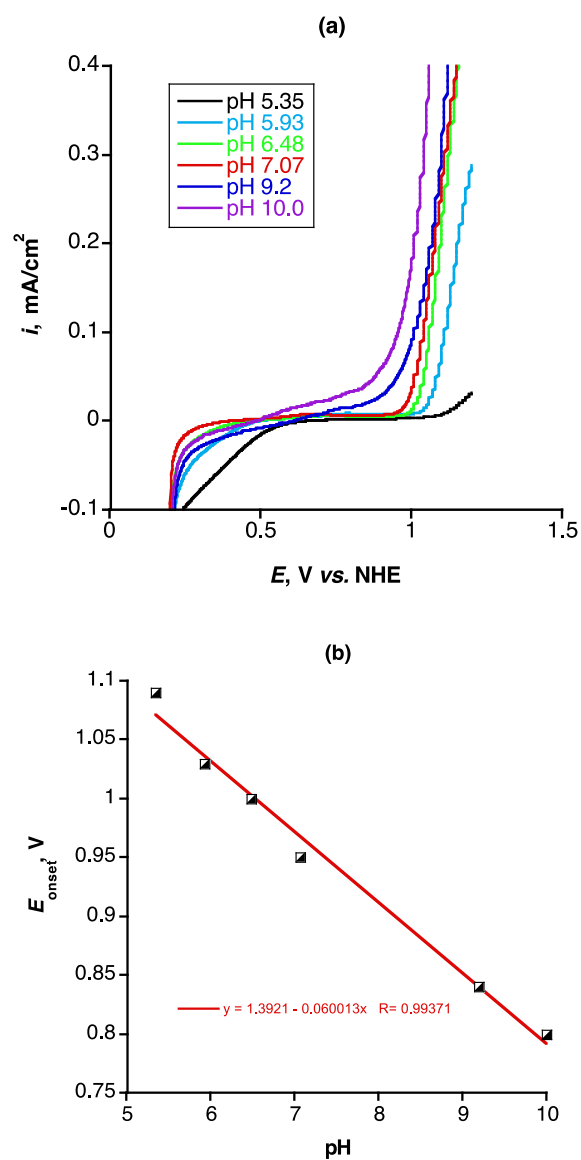


Figure S8. (a) LSVs at 5 mV/s scan rate of FTO/EMI CaMn-Oxide (red line) in a 0.1 M KPi buffer solutions of different pHs (b) Onset potential of the water oxidation peak (E_{onset}) and pHs relationship.

- 1 Z. N. Zahran, E. A. Mohamed, T. Ohta and Y. Naruta, *ChemCatChem*, 2016, **8**, 532–535.