

– Supporting Information –

Selective Hydrogen Evolution on Manganese Oxide Coated Electrodes: New Cathodes for Sodium Chlorate Production

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MnO_x/Ti electrode formation by the thermal decomposition of Mn(NO₃)₂ precursor

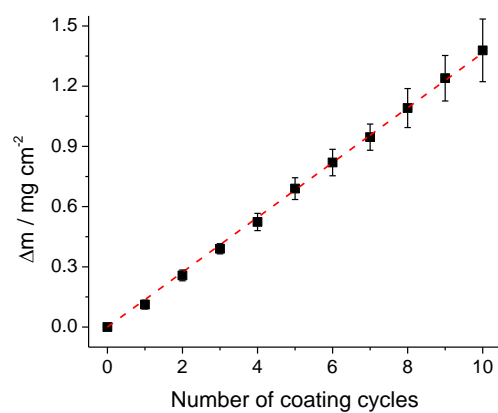


Figure S1. The cumulative weight increase during the subsequent layer coating cycles (brush-coating $V \approx 50 \mu\text{l}$ Mn(NO₃)₂ precursor, drying at $T_1 = 60^\circ\text{C}$ for $t_1 = 10$ min, annealing at $T_2 = 400^\circ\text{C}$ for $t_2 = 10$ min).

SR-XPS study of the electrode composition

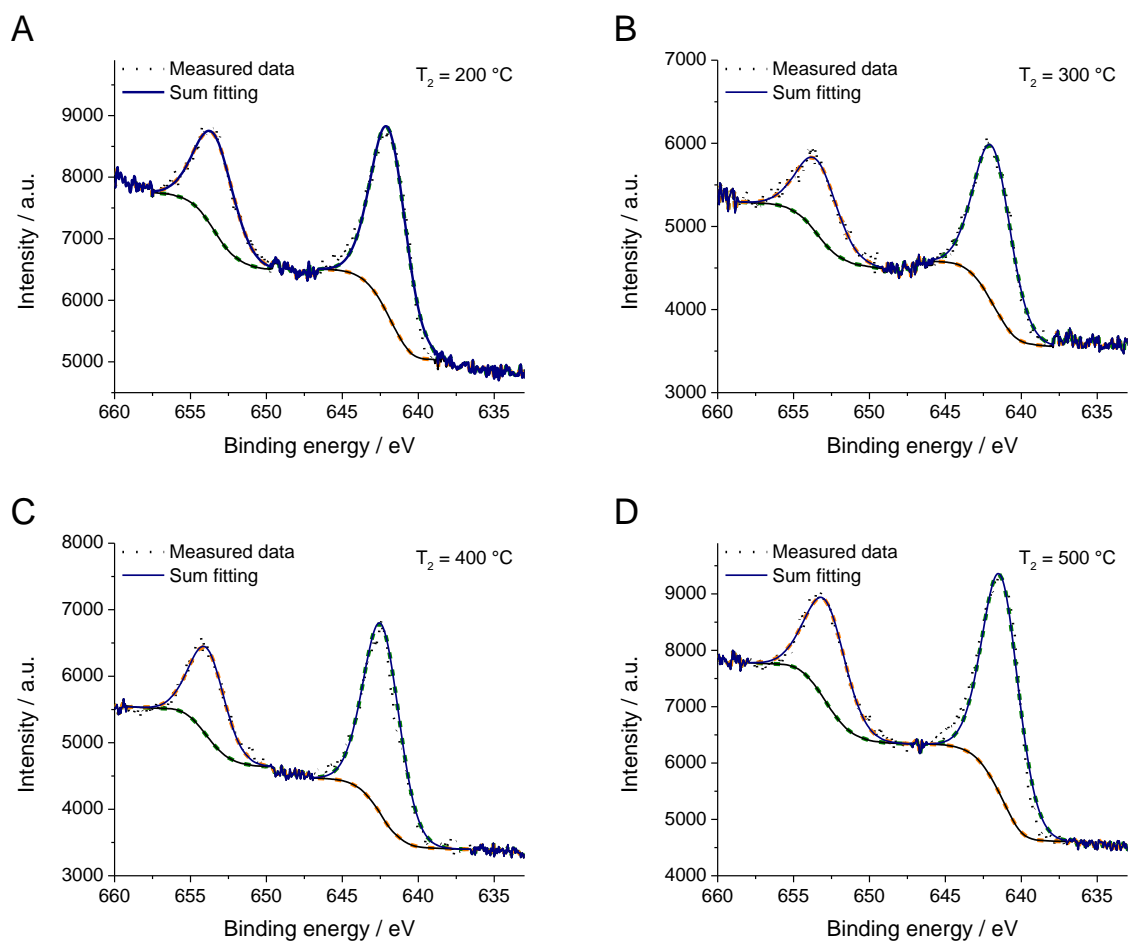


Figure S2. SR-XPS Mn 2p spectra for the MnO_x/Ti electrodes formed at different annealing temperatures (1.5 mg cm⁻² MnO_x loading): (A) 200 °C, (B) 300 °C, (C) 400 °C and (D) 500 °C.

Table S1. O-to-Mn atomic ratios in the MnO_x samples formed at different annealing temperatures (1.5 mg cm⁻² MnO_x loading), as determined from the SR-XPS measurements, as illustrated in **Figure S2**.

Annealing Temperature	Electrochemical Polarization	O-to-Mn ratio
200 °C	No	1.98
300 °C	No	1.76
400 °C	No	1.78
500 °C	No	1.76
400 °C	Yes	2.00
500 °C	Yes	2.15

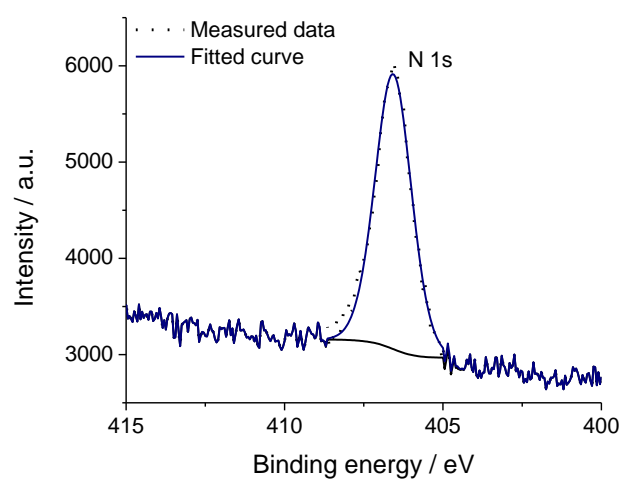


Figure S3. SR-XPS spectrum of a MnO_x-200-1.5 electrode, shown for the N 1s binding energy region.

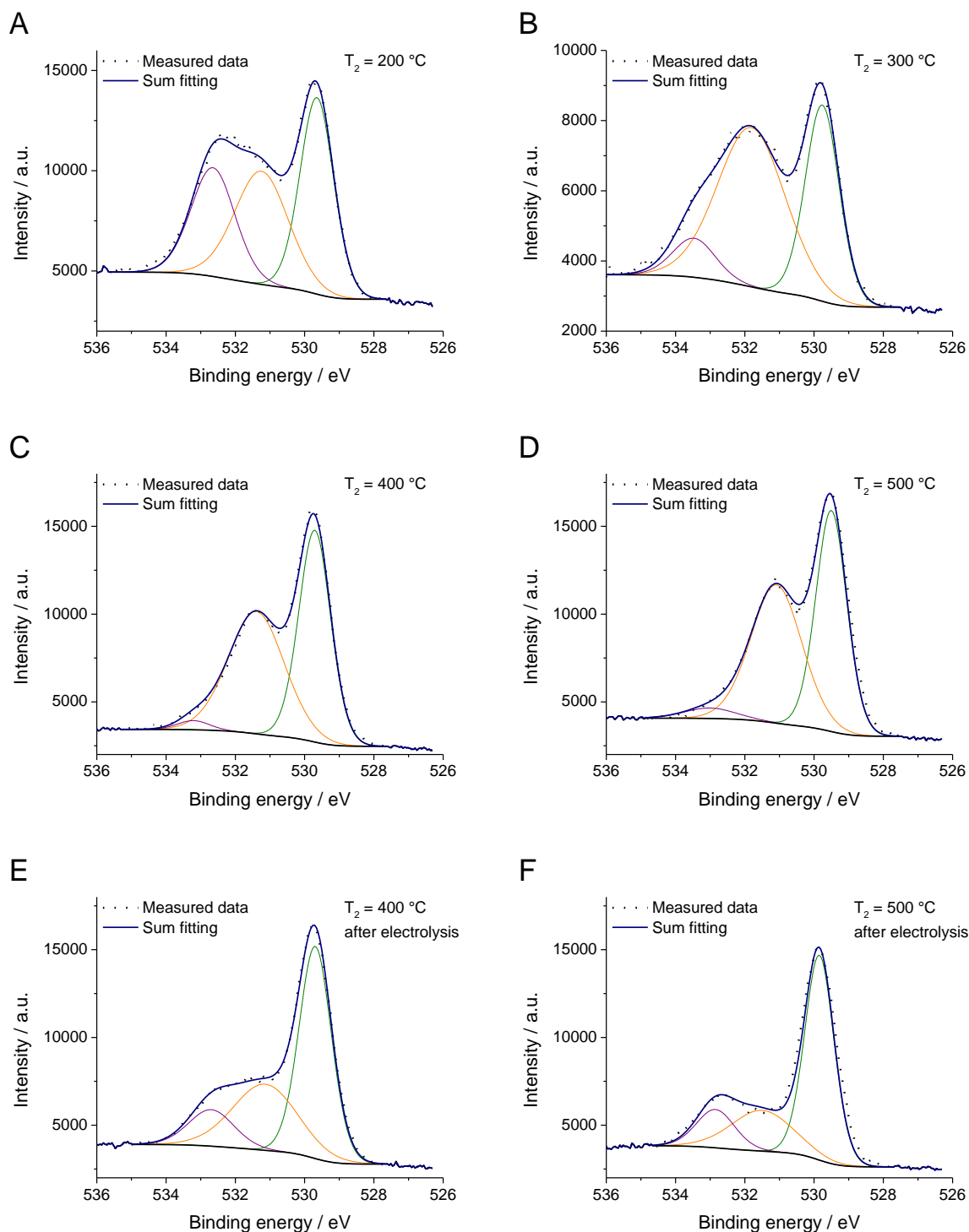


Figure S4. SR-XPS O 1s spectra of the MnO_x/Ti electrodes formed at different annealing temperature (1.5 mg cm^{-2} MnO_x loading): (A) $200\text{ }^{\circ}\text{C}$, (B) $300\text{ }^{\circ}\text{C}$, (C) $400\text{ }^{\circ}\text{C}$, (D) $500\text{ }^{\circ}\text{C}$, (E) $400\text{ }^{\circ}\text{C}$ after subjecting to electrochemical polarization, and (F) $500\text{ }^{\circ}\text{C}$ after subjecting to electrochemical polarization in an 80 mM NaOCl and 2 M NaCl containing solution.

Morphology of the MnO_x/Ti electrodes formed at different annealing temperatures

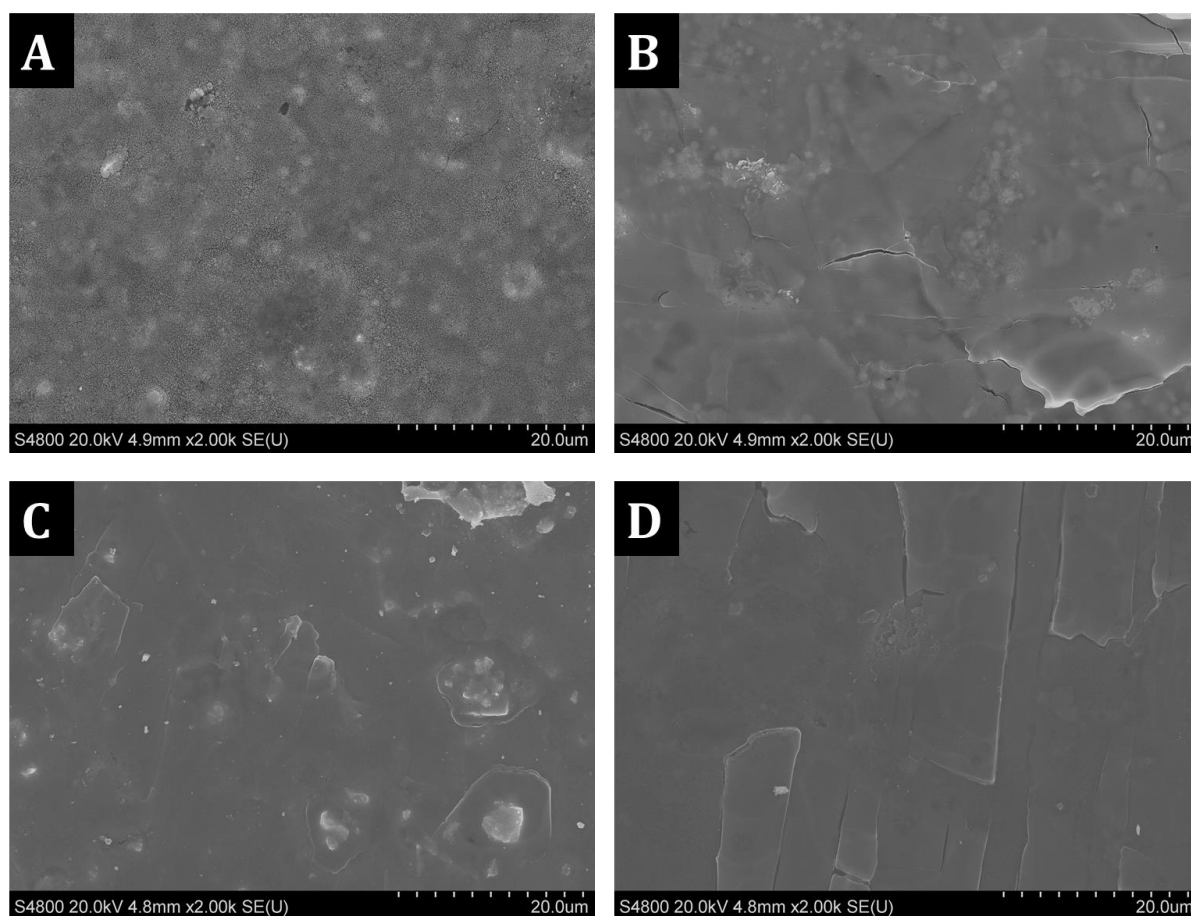


Figure S5. SEM images taken of the MnO_x/Ti electrodes formed at different annealing temperatures (A) $T_2 = 200\text{ }^\circ\text{C}$, (B) $T_2 = 300\text{ }^\circ\text{C}$ (C), $T_2 = 400\text{ }^\circ\text{C}$ and (D) $T_2 = 500\text{ }^\circ\text{C}$, with the same catalyst loading ($\sim 1.5\text{ mg cm}^{-2}$).

Electrochemical characterization of the formed MnO_x/Ti electrodes

The relative electrochemically active surface area of the formed MnO_x layers was addressed by cyclic voltammetric measurements, in a potential window where no Faradaic reactions occur (**Figure S6A**), while the resistance of the layers was studied by electrochemical impedance spectroscopy (**Figure S6B**) performed at an electrode potential ($E = +300$ mV) in this range.

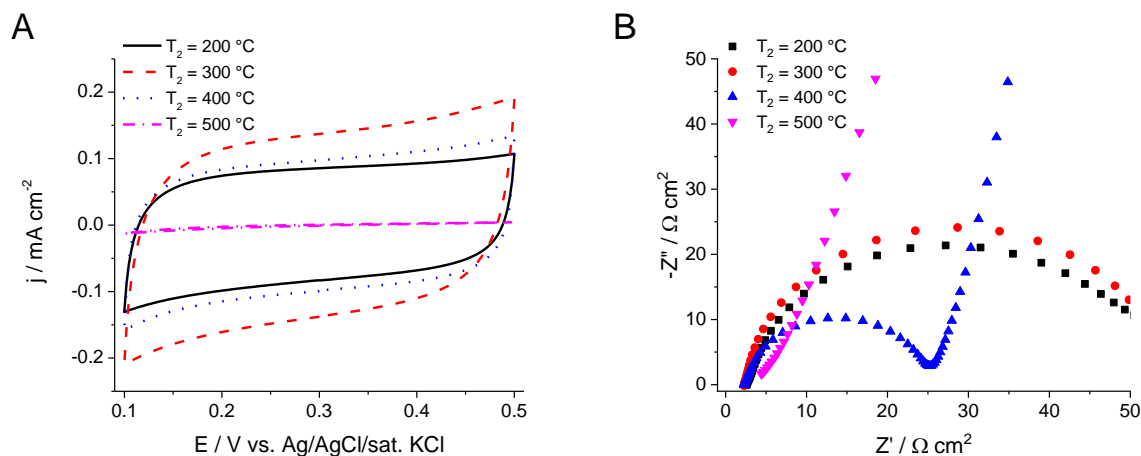


Figure S6. (A) Cyclic voltammograms ($\nu = 10$ mV s⁻¹) of MnO_x/Ti electrodes with 1.5 mg cm⁻² MnO_x amount, prepared by applying different annealing temperatures. (B) EIS spectra of the same layers as in (A), recorded at $E = +300$ mV. Both set of experiments were performed in argon purged 2 M NaCl solution.

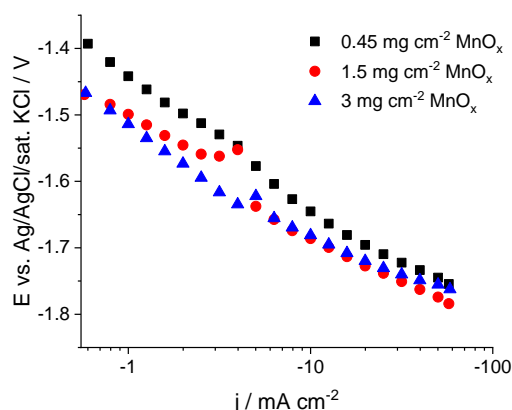


Figure S7. IR-corrected polarization curves with MnO_x/Ti electrodes prepared at $T = 500$ °C annealing temperatures with different MnO_x amounts. The measurements were performed in N₂ purged 2 M NaCl solution.

Effect of catalyst loading on the morphology of the MnO_x/Ti electrodes formed at 500 °C annealing temperature.

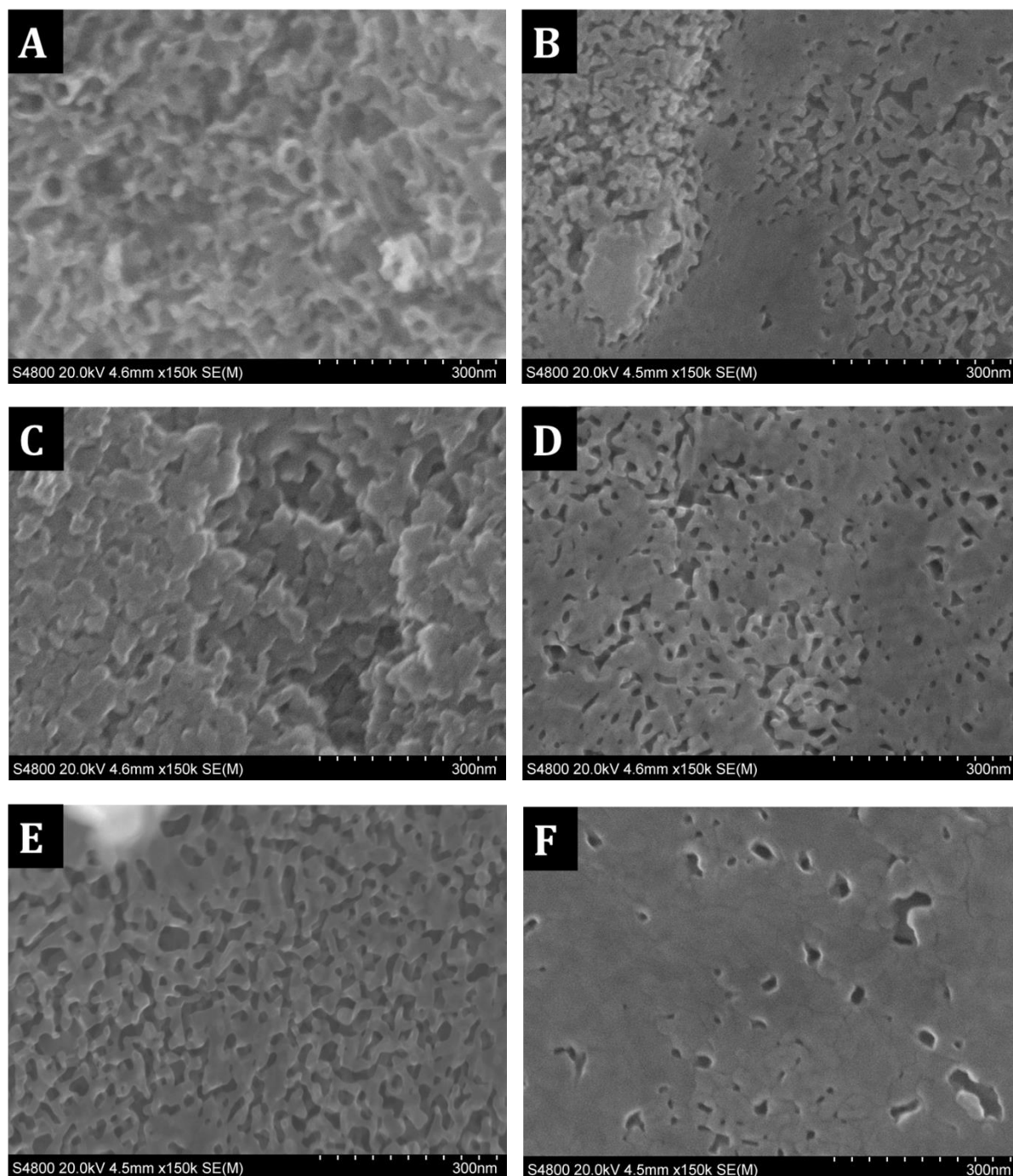


Figure S8. SEM images of MnO_x/Ti electrodes formed at $T_2 = 500$ °C annealing temperature, with increasing MnO_x loading from (A) to (F) (0.15, 0.45, 0.75, 1.5, 2.25 and 3.0 mg cm^{-2} , accordingly).