Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information

Nanolayered manganese oxide: Insights from inorganic electrochemistry†

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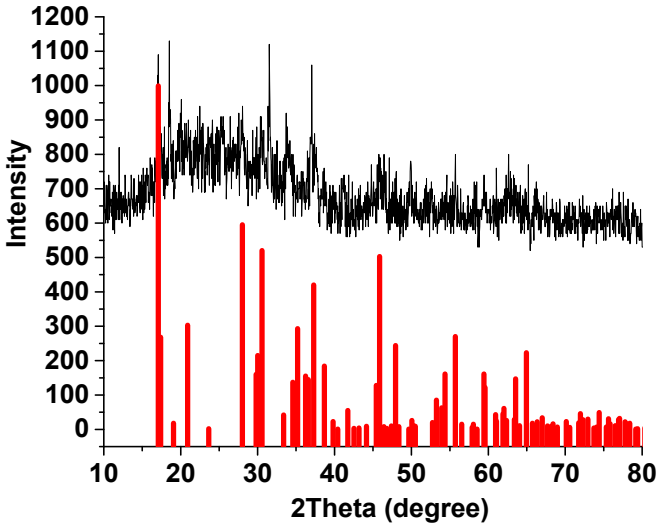

Figure S1 XRD diffractograms for the $Ca_2Mn_3O_8$ (reference code: 01-073-2290) (red) and Mn-Ca oxides (black) calcined at 600 ^oC.

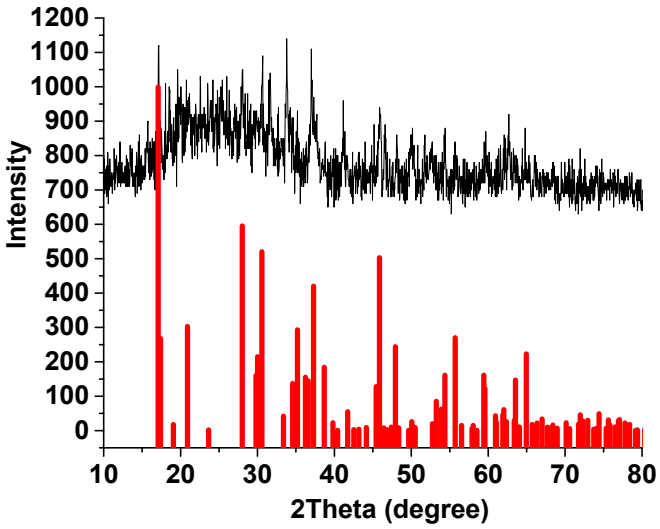

Figure S2 XRD diffractograms for the $Ca_2Mn_3O_8$ (reference code: 01-073-2290) (red) and Mn-Ca oxides (black) calcined at 700 ^oC.

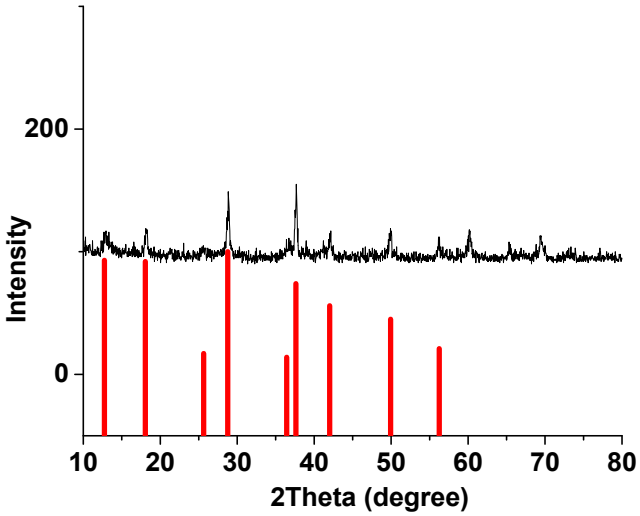

Figure S3 XRD diffractograms for $H_{1.63}K_{0.37}Mn_8O_{16}\cdot 24H_2O$ (reference code: 00-049-0677) (red) and Mn-K oxides (black) calcined at 400 ^{o}C.

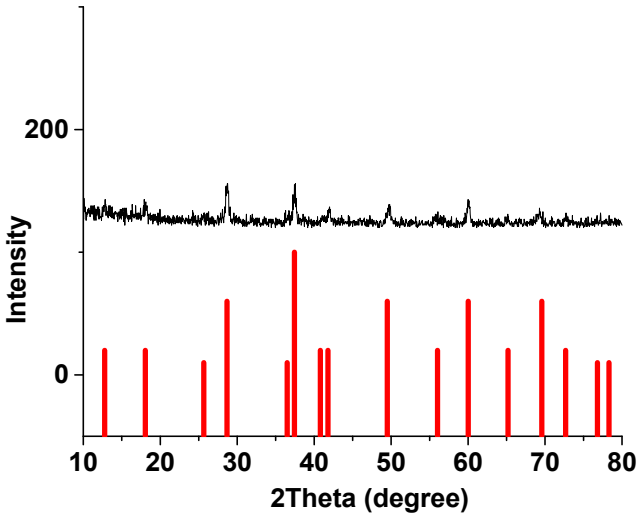

Figure S4 XRD diffractograms for cryptomelane (KMn_8O_{16}, reference code: 00-006-0547) (red) and Mn-K oxides (black) calcined at 500 ^{o}C.

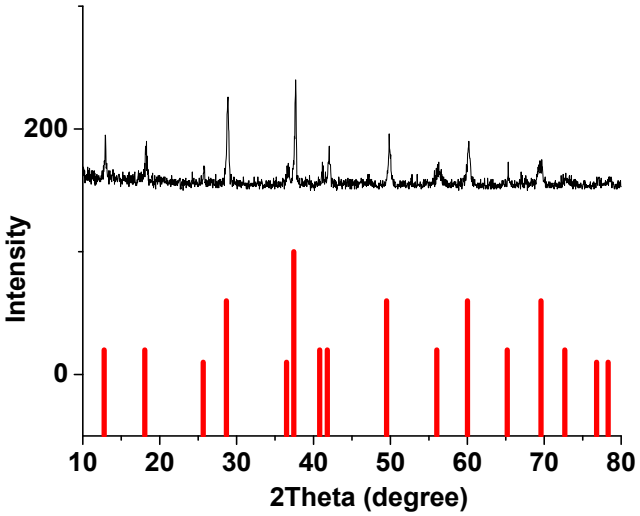

Figure S5 XRD diffractograms for cryptomelane ($KMn_8O_{16,}$ reference code: 00-006-0547) (red) and Mn-K oxides (black) calcined at 600 ^{o}C.

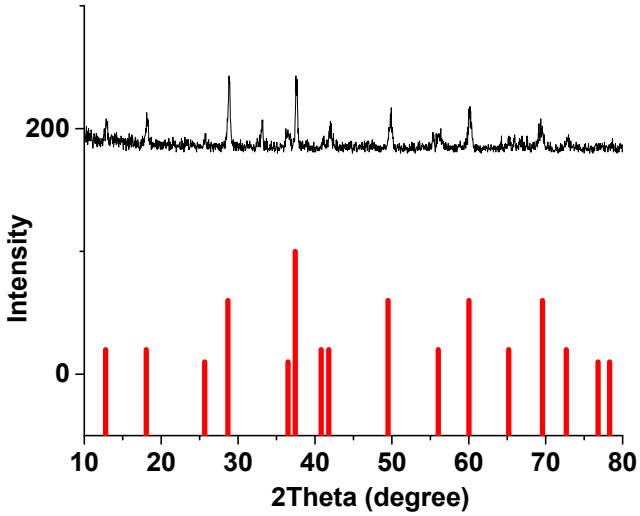

Figure S6 XRD diffractograms for cryptomelane ($KMn_8O_{16,}$ reference code: 00-006-0547) (red) and Mn-K oxides (black) calcined at 700 ^{o}C.

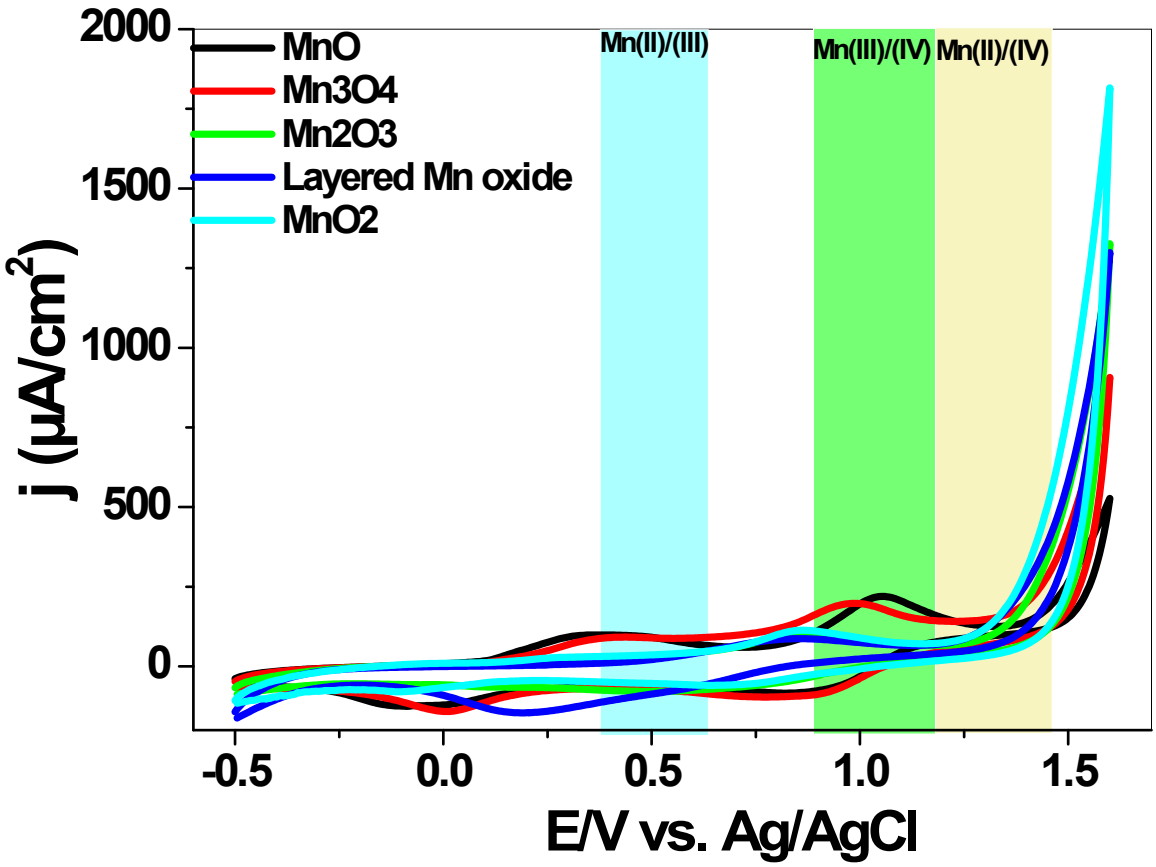

Figure S7 CV for different Mn oxides. 20 µL of Mn oxides in water (1 mg/mL) was dripped on the FTO electrode and dried at 60 °C. Then, 10 µL of 0.5 wt % Nafion solution was cast on the surface of the FTO electrode (1.0 cm^2). A three-electrode system includes an FTO slide, Pt foil as counter-electrode and $Ag|AgCl|KCl_{sat}$ as reference electrodes were applied for investigation of the electrochemical properties of the catalyst (room temperaure, $LiClO_4$ (0.25 M), pH=6.3 the scan rate was 50 $mV.s^{-1}$). The calcination temperature for layered Mn oxide (Mn-Ca oxide) was 300 ^oC. Other Mn oxides were purchased from the Sigma-Aldrich Company.

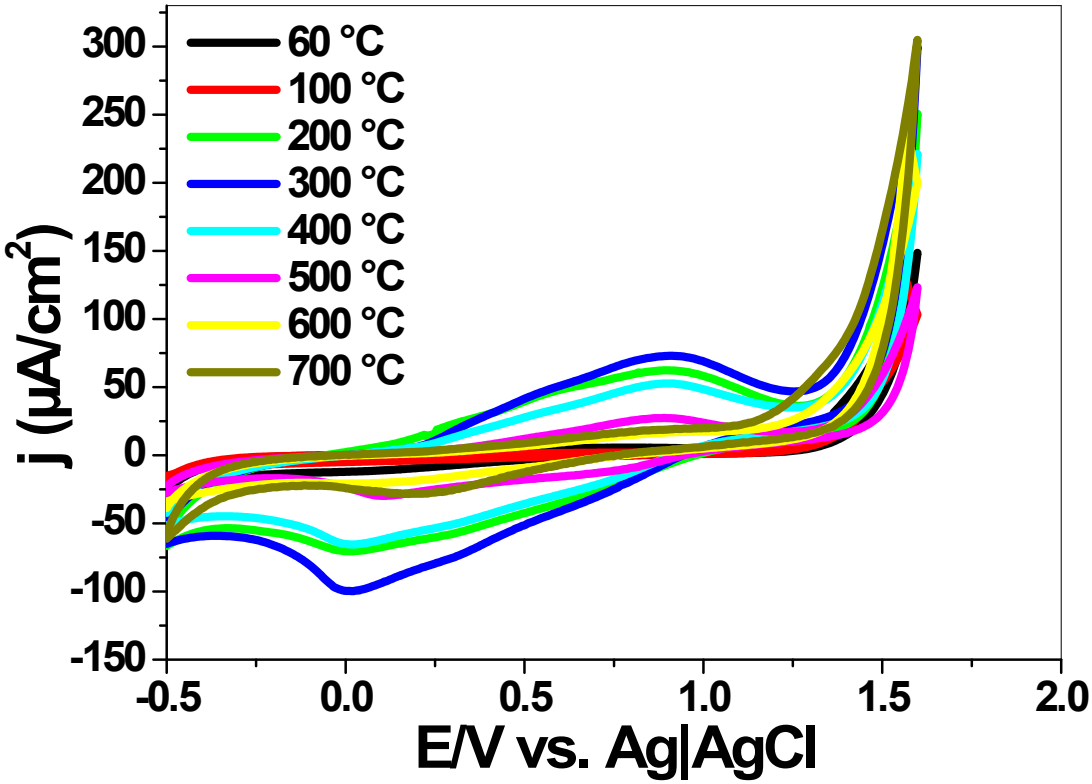

Figure S8 The effect of different calcination temperatures on CVs of nanolayered Mn-Ca oxide. 30 µL of Mn oxide dispersed in water (1mg/mL) was dripped on the FTO electrode and dried at 60 °C. Then, 10 µL of 0.5 wt % Nafion solution was cast on the surface of the FTO electrode (1.0 cm^2). A three-electrode system includes an FTO slide, Pt foil as counter and $Ag|AgCl|KCl_{sat}$ as reference electrodes and was applied for investigation of the electrochemical properties of the catalyst (room temperaure, $LiClO_4$ (0.25 M), pH=6.3; scan rate: 50 $mV.s^{-1}$).

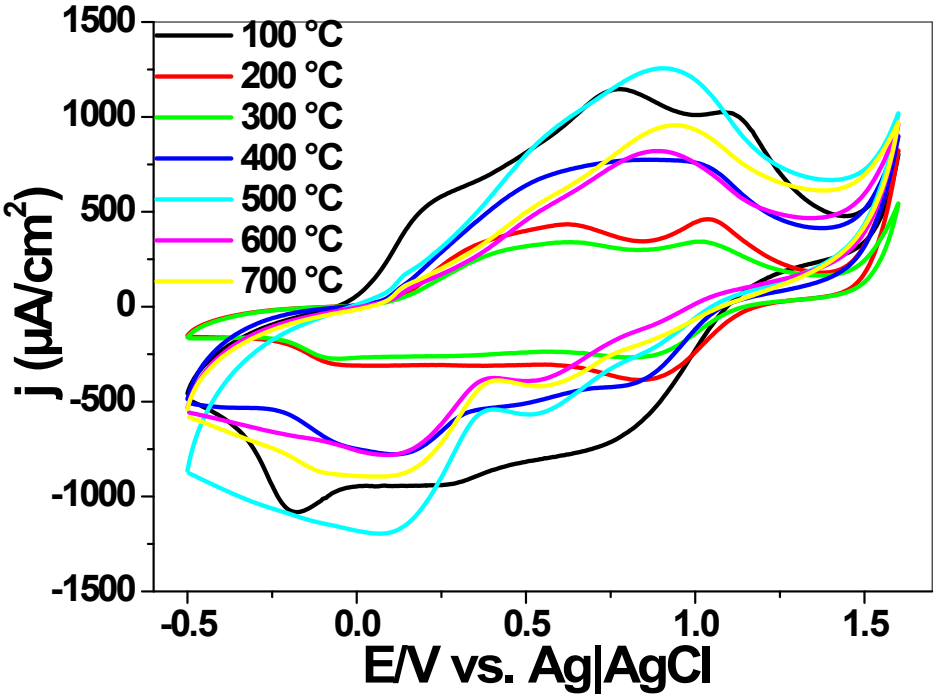

Figure S9 The effect of different calcination temperatures on CVs of nanolayered Mn-K oxide on FTO. A three-electrode system includes an FTO slide, Pt foil as counter-electrode and $Ag|AgCl|KCl_{sat}$ as reference electrode. This system was applied for investigation of the electrochemical properties of the catalyst (room temperaure, $LiClO_4$ (0.25 M), pH=6.3; scan rate: 50 $mV.s^{-1}$).

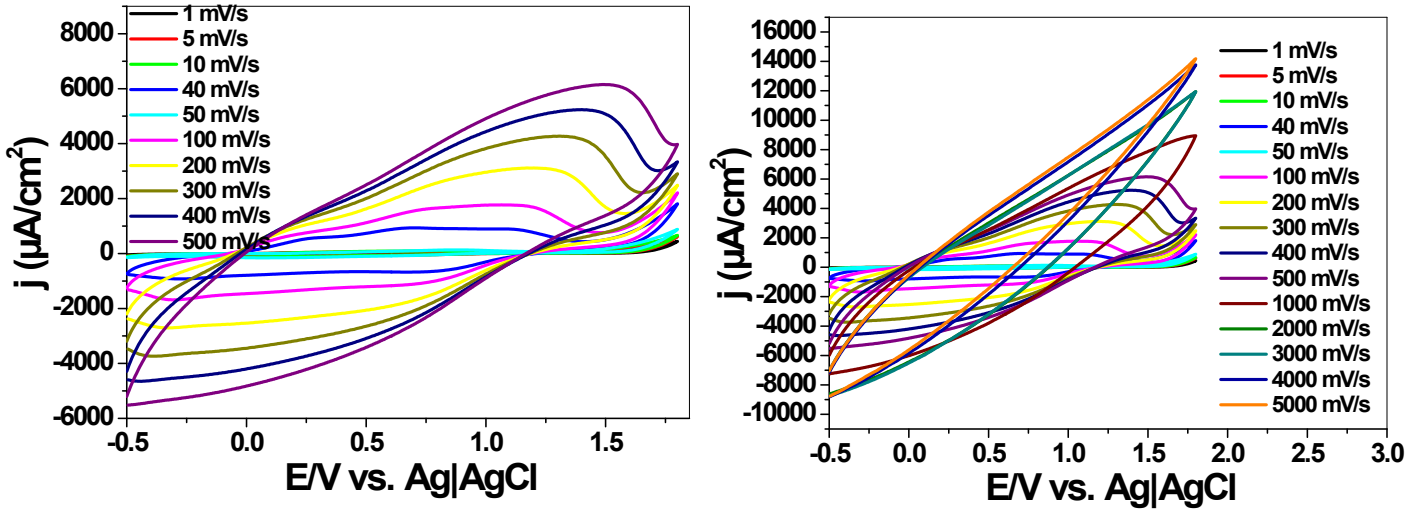

Figure S10 The effect of different scan rates for CVs of nanolayered Mn-K oxide on FTO. A three-electrode system includes an FTO slide, Pt foil as counter-electrode and $Ag|AgCl|KCl_{sat}$ as reference electrode (1.0 cm^2). This system was applied for investigation of the electrochemical properties of the catalyst (room temperaure, $LiClO_4$ (0.25 M), pH=6.3). Nanolayered Mn-Ca oxide/Nafion is not very stable under these conditions.

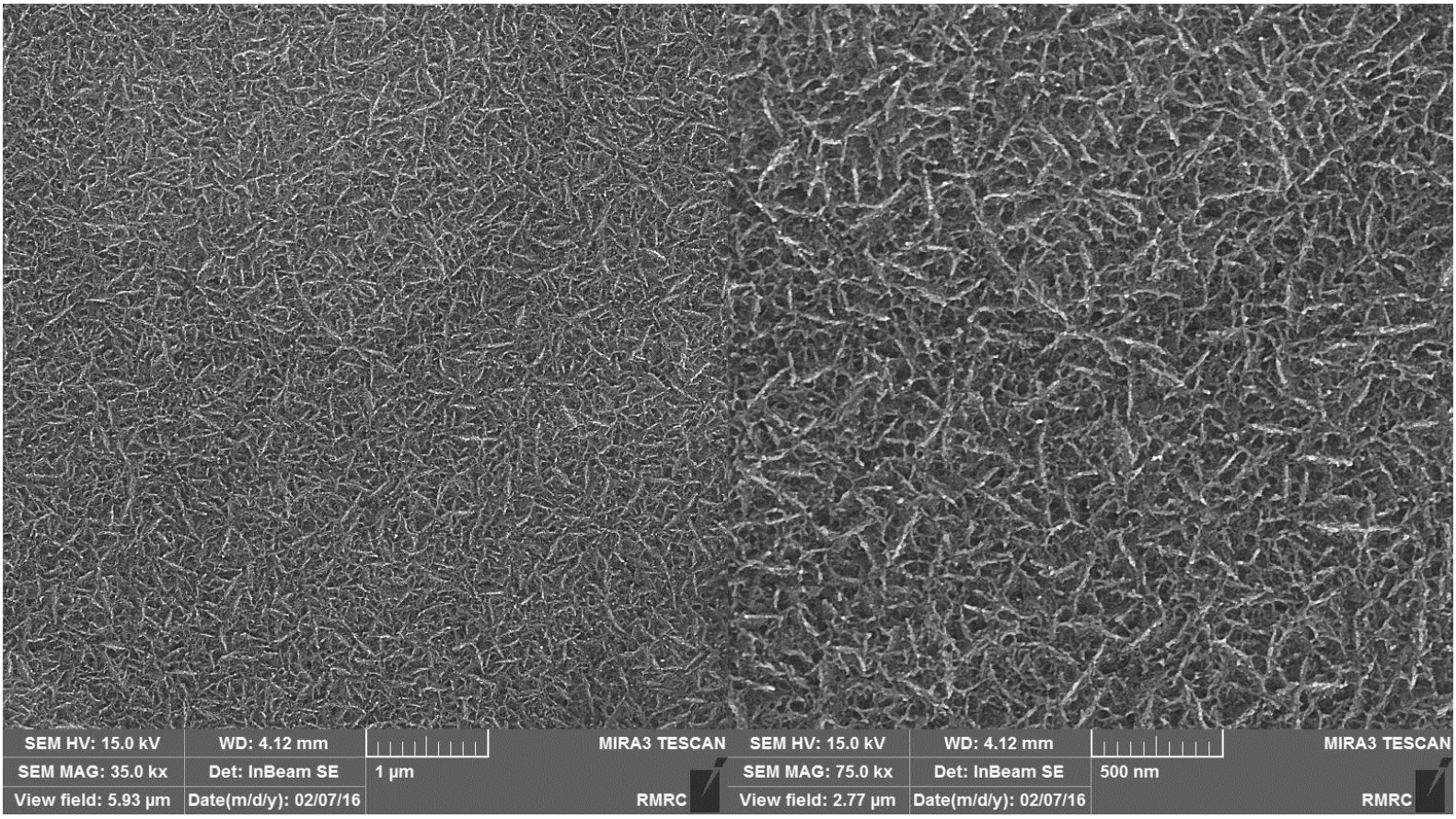

Figure S11 SEM images of electrodeposited Mn oxide on FTO from $Mn(ClO_4)_2$ (300.0 mg in 20.0 mL water) at 1.2V vs. $Ag|AgCl|KCl_{sat}$; counter-electrode: Pt foil and under chronoamperometric condition.

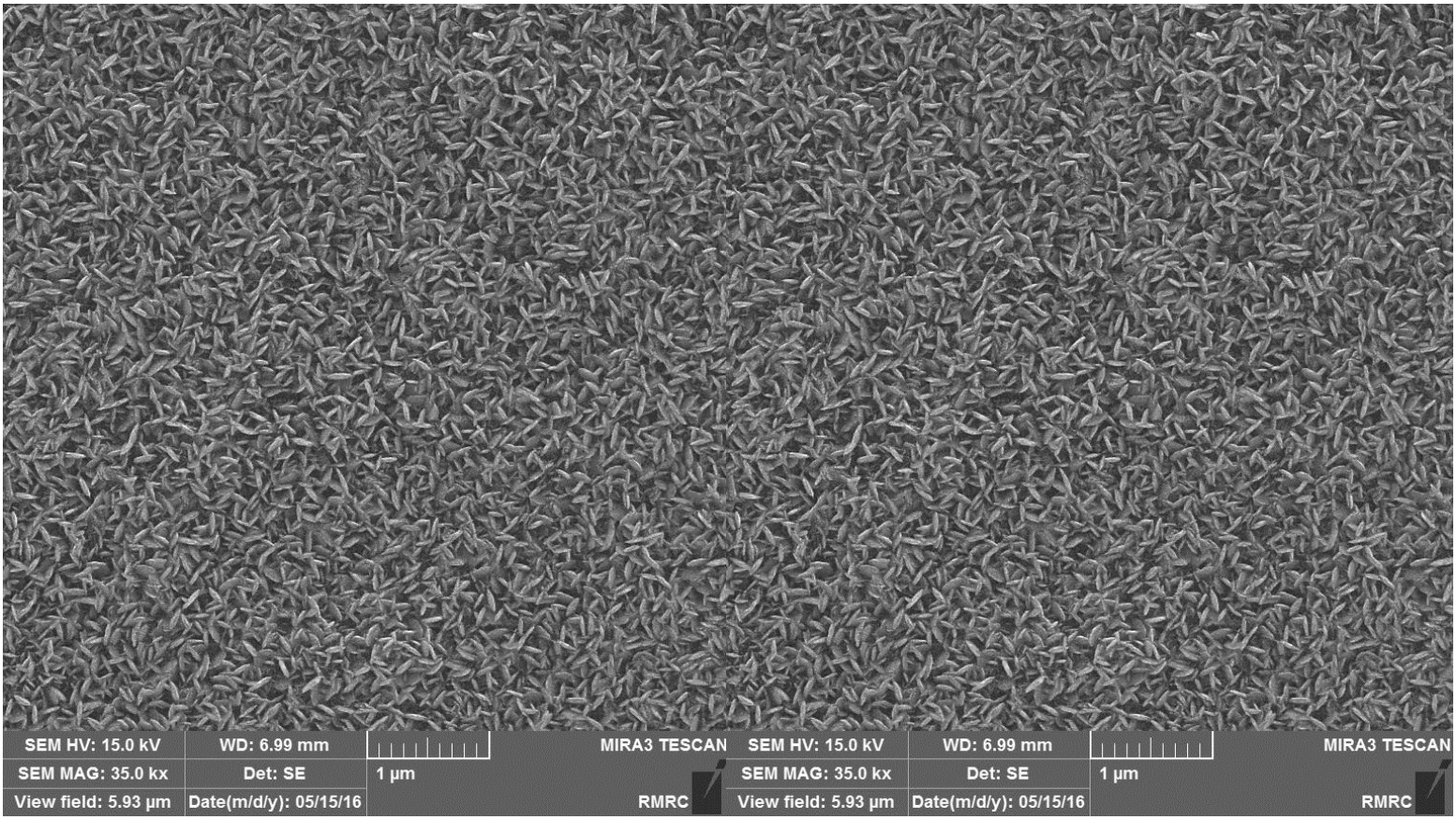

Figure S12 SEM images of electrodeposited Mn oxide on FTO from $Mn(ClO_4)_2$ (300.0 mg in 20.0 mL aqueous $LiClO_4$ (0.25 M)) at 1.2V vs. $Ag|AgCl|KCl_{sat}$; counter-electrode: Pt foil and under chronoamperometric condition.

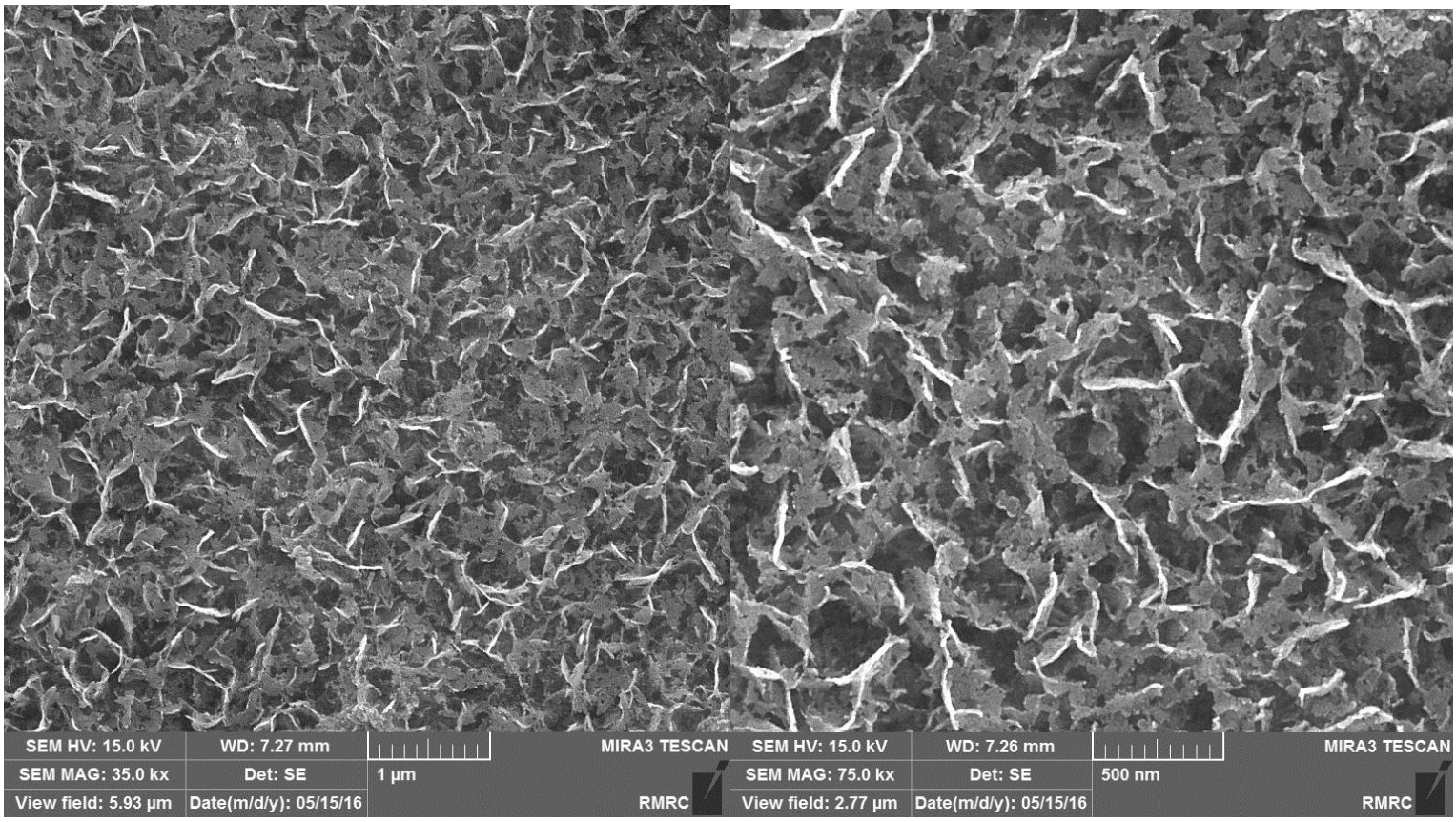

Figure S13 SEM images of electrodeposited Mn oxide on FTO from $Mn(ClO_4)_2$ (300.0 mg in 20.0 mL aqueous $LiClO_4$ (0.25 M)) under cyclic voltammetric condition (-0.5-1.6 vs. $Ag|AgCl|KCl_{sat}$; counter-electrode: Pt foil).

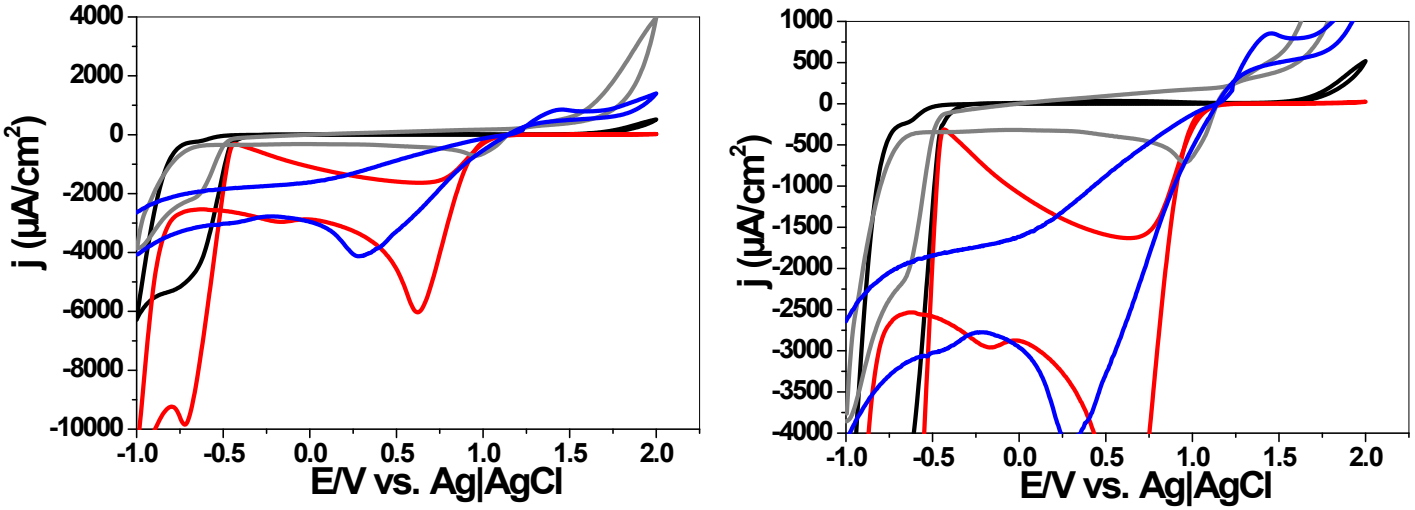

Figure S14 The CV of FTO in the presence of HNO_3 (0.1 M) (black) and CAN (red), and Mn-K oxide on FTO in the presence of HNO_3 (0.1 M) (gray) and CAN (blue). A three-electrode system includes an FTO slide, Pt foil as counter-electrode and $Ag|AgCl|KCl_{sat}$ as reference electrode. This system was applied for investigation of the electrochemical properties of the catalyst (scan rate = 100 $mV.s^{-1}$, room temperature, $LiClO_4$ (0.25 M)). Nanolayered Mn-Ca oxide/nafion is not very stable under these conditions.

Table S1 Onset potentials for water oxidation by layered Mn-Ca oxides ($LiClO_4$ (0.25 M), pH=6.3). A three-electrode system includes an FTO slide, Pt foil as counter-electrode and $Ag|AgCl|KCl_{sat}$ as reference electrode (1.0 cm^2). This system was applied for investigation of the electrochemical properties of the catalyst (room temperaure, $LiClO_4$ (0.25 M), pH=6.3).

Compounds	Onset potentials (vs. $AgIAgCl_{sat}$)
MnO	1.53
Mn_3O_4	1.50
Mn_2O_3	1.49
MnO_2	1.47
Layered Mn oxide (60)	1.51
Layered Mn oxide (100)	1.49
Layered Mn oxide (200)	1.48
Layered Mn oxide (300)	1.46
Layered Mn oxide (400)	1.48
Layered Mn oxide (500)	1.52
Layered Mn oxide (600)	1.51
Layered Mn oxide (700)	1.5