Electronic Supplementary Information: electro-precipitation via oxygen reduction: a new technique for thin film manganese oxide deposition

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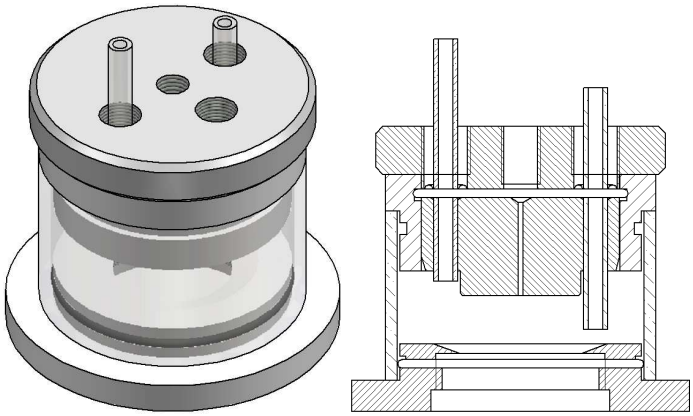
The electrochemical behavior was investigated by cyclic voltammetry without dissolved oxygen in solution, thus only the Mn-ions are studied. Cyclic voltammetry was measured at room temperature, using a platinum disk (ϕ = 1.5 mm) as working electrode. First of all the electrochemical window of DMSO was measured without the presence of manganese ions (Figure S4, red). It can be seen that DMSO is stable over a wide potential range from -4.0 to +1.0 V vs. Ag/Ag^+. When 0.1 M of Mn^{2+}-ions are added in the form of $Mn(Tf_2N)_2$, cyclic voltammograms were scanned from open circuit potential (OCP) to the negative vertex potential, to the positive vertex potential and back to the OCP at a scan rate of 50 mV s^{-1}. Figure S4 shows one reduction peak at -0.97 V vs. Ag/Ag^+ with a current density of -2.4 $\times$ 10^{-2} A dm^{-2} and one oxidation peak (a_1) at -0.37 V vs. Ag/Ag^+ and 0.68 $\times$ 10^{-2} A dm^{-2}. These peaks correspond with the deposition of Mn^0 from Mn^{2+} and the dissolution according to reaction. The manganese metal deposition was confirmed by applying a potential of -3.0 V vs. Ag/Ag^+ for 300 s, resulting in a cauliflower-like deposit (Figure S5). The electro-precipitation of Mn_xO_y was investigated by EQCM using cyclic voltammetry (Figure S6) and XRD (Figure S7 and S8. In Figure S7 the integrated intensity at 26° – 28° was plotted, it can be seen that the intensity decreases with increasing temperature and increases again upon cooling down. The temperature at which Mn_2O_3 starts to crystallize is 495.8C, here the intensity suddenly increases (Figure S8).



(a) (b)

Fig. 1 Design of the EQCM setup: the lid has four entries, an oxygen inlet and outlet and two feed-throughs for the reference and counter electrode. The cell is sealed with Kalrez O-rings and can be screwed on a commercial Maxtex RQCM-crystal holder.

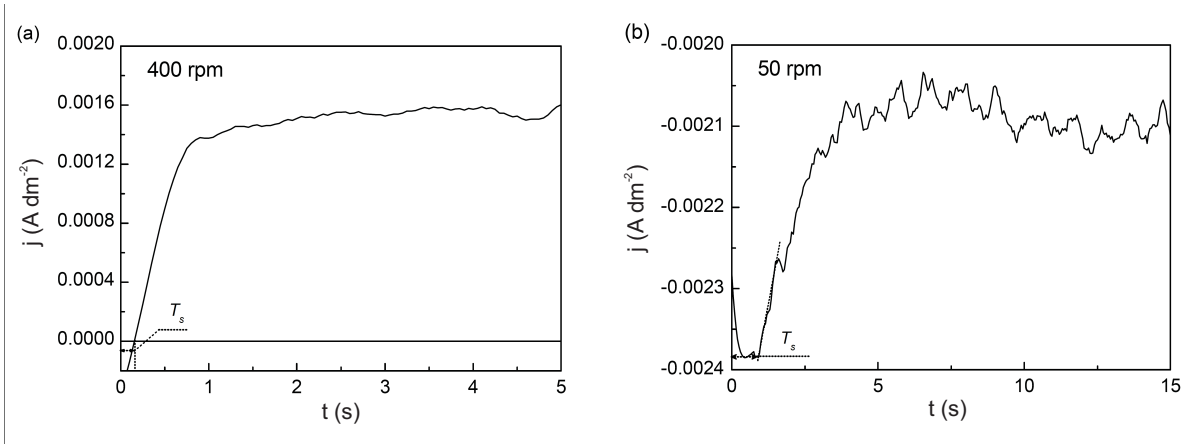


Fig. 2 The transient time in an oxygen-saturated 1 M TBAP solution in DMSO at room temperature. The disk potential was stepped from open circuit to -1.6 V (vs. Ag/Ag^{+}) and the ring potential was held at (a) +0.3 V or at (b) -1.6 V (vs. Ag/Ag^{+}).

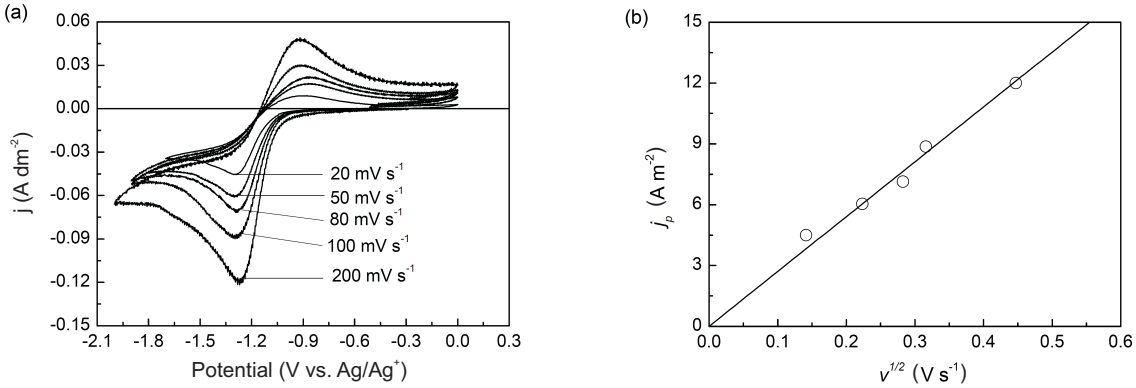


Fig. 3 Cyclic voltammograms of the oxygen-saturated 1 M TBAP solution in DMSO with different scan rates (a) and the plot of peak current density with the square root of scan rate (b). The working electrode was a glassy carbon disk (ϕ = 1 mm), and the counter electrode was a platinum coil.

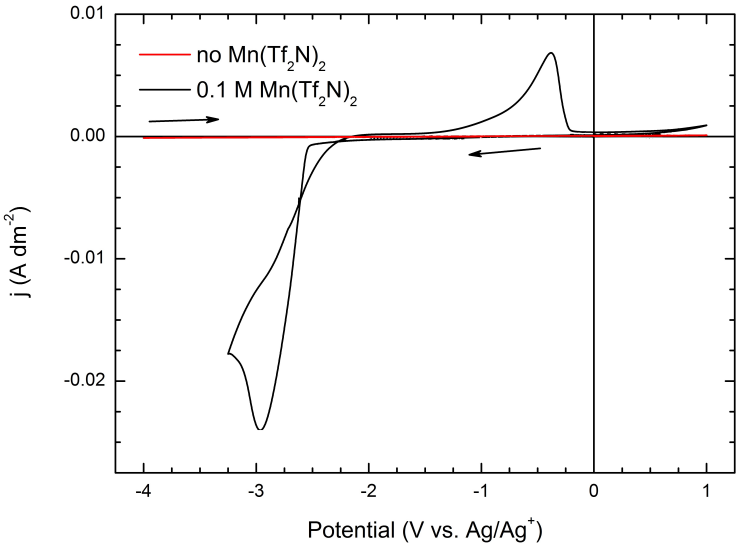
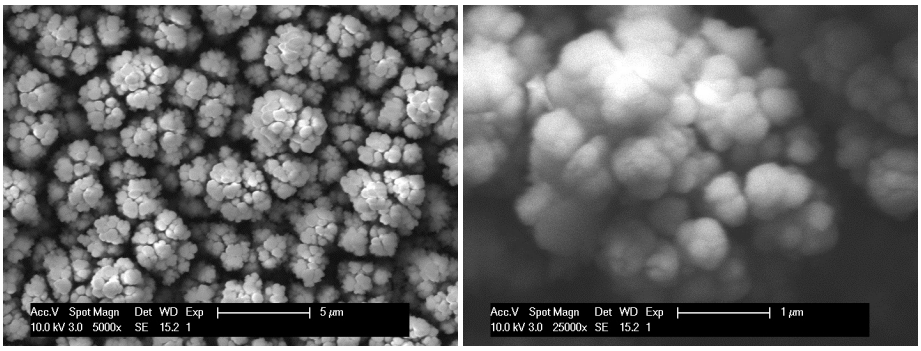
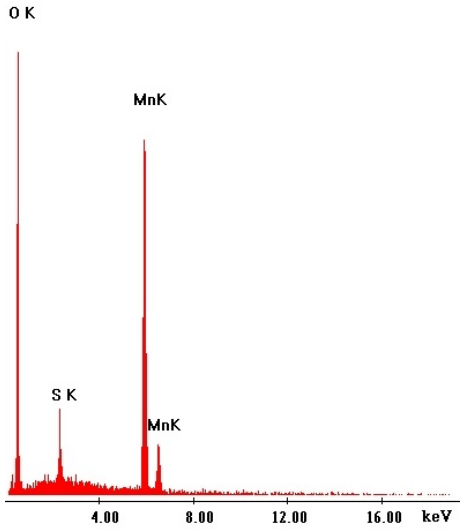


Fig. 4 Cyclic voltammograms of a DMSO solution containing no manganese salt (a, red) or 0.1 M $Mn(Tf_2N)_2$ (a, black). The working electrode was a platinum disk (ϕ = 1.5 mm) The real reference electrode was a silver wire in a glass tube with fritt, filled with 0.1 M $Ag(NO_3)$ and 1 M $LiTf_2N$ in DMSO. The counter electrode was a platinum coil and the scan rate was 50 mV s^{-1}.



(a) (b)



(c)

Fig. 5 SEM and EDX analysis of a potentiostatic deposition of manganese from a 0.1 M $Mn(Tf_2N)_2$ DMSO solution. The potential was held at -3.0 V vs. Ag/Ag^+ for 300 s and a platinum coated silicon wafer was used as substrate while the electrolyte was stirred.

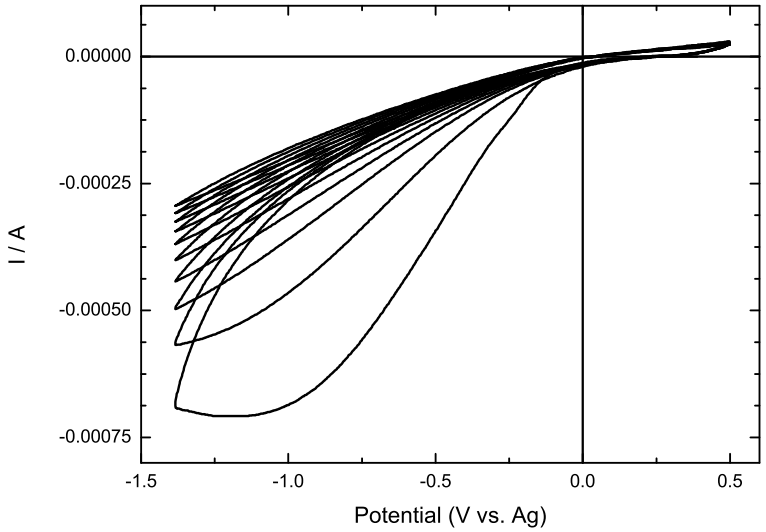


Fig. 6 Cyclic voltammograms of a DMSO solution with dissolved oxygen and 0.1 M $Mn(Tf_2N)_2$. The working electrode was an AT cut platinum coated quartz crystal with an active surface area of 1.27 cm^2. The reference electrode was a silver wire directly immersed in the electrolyte. The counter electrode was a platinum coil and the scan rate was 50 mV s^{-1}.

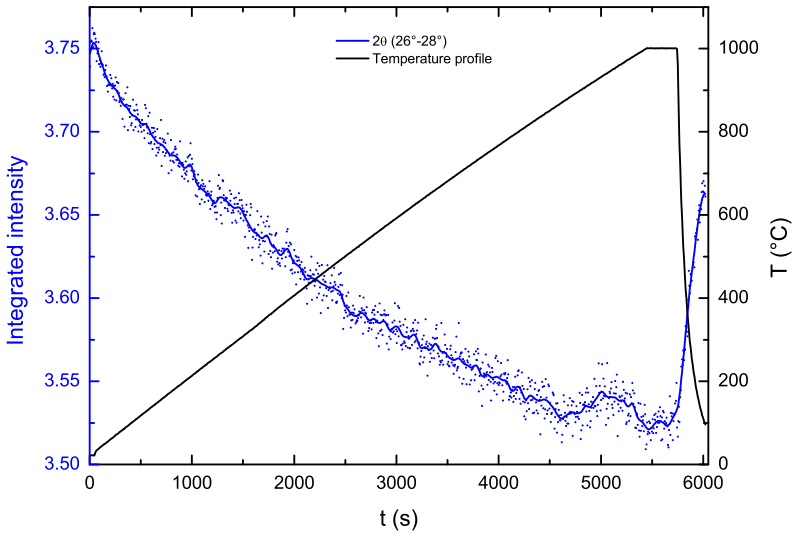


Fig. 7 Integrated intensity of the XRD pattern of MnO_2 at 26° – 28°. The intensity increases upon cooling at 5740 s.

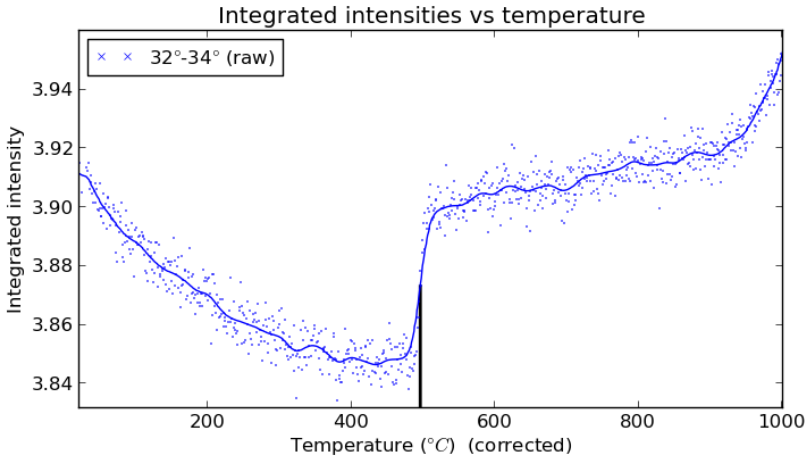


Fig. 8 Integrated intensity of the XRD pattern of Mn_2O_3 at $32^\circ - 34^\circ$. The intensity increases at 496 C, where Mn_2O_3 starts to crystallize.

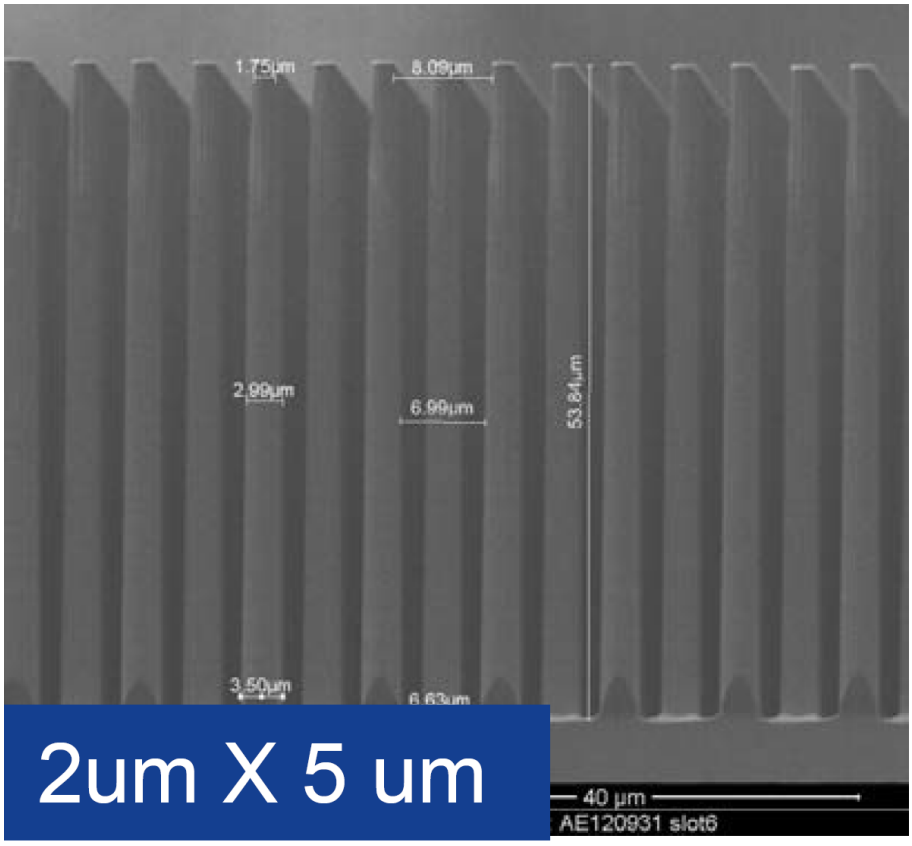


Fig. 9 3D silicon pillars coated with TiN as current collector.

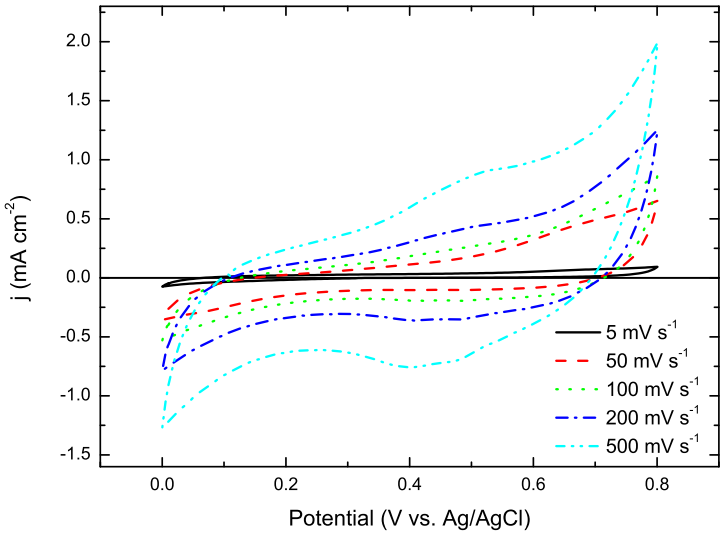


Fig. 10 Capacitance measured via cyclic voltammetry in 0.5 M K_2SO_4 aqueous electrolyte using a Pt counter electrode and Ag/AgCl reference electrode. A Mn_xO_y thin film of approx. 80 nm was deposited on a planar Pt working electrode. The capacitance was measured at various scan rates from 5 - 500 mV s^{-1}.

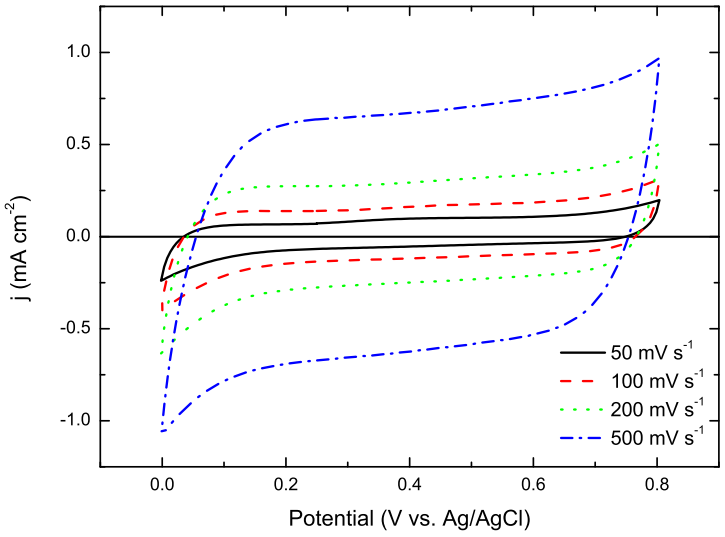


Fig. 11 Capacitance measured via cyclic voltammetry in 0.5 M K_2SO_4 aqueous electrolyte using a Pt counter electrode and Ag/AgCl reference electrode. A Mn_xO_y thin film was deposited on a planar working electrode coated with carbon nanosheets (height 20 - 70 nm). The capacitance was measured at various scan rates from 50 - 500 mV s^{-1}.

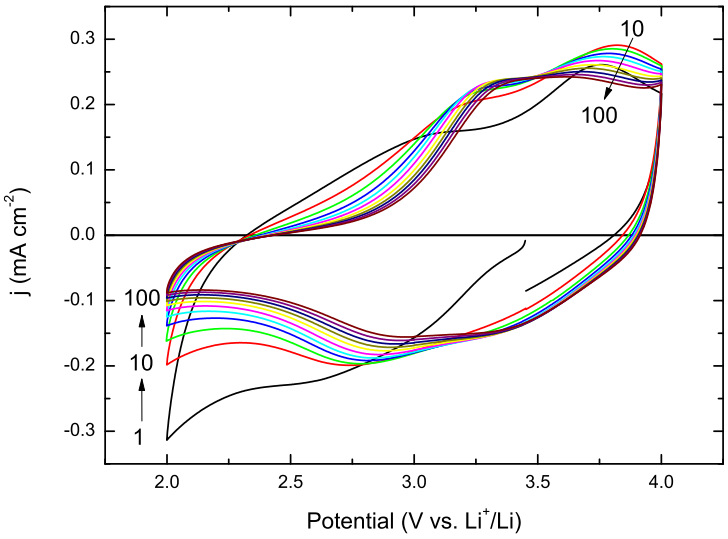


Fig. 12 Lithiation/delithiation of 300 nm Mn_xO_y thin film on a planar working electrode coated with carbon nanosheets (height 2 μm) using cyclic voltammetry. A lithium reference and counter electrode was used and as electrolyte a 1 M $LiClO_4$ in anhydrous propylene carbonate solution.