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Supplementary Information for:

Nanoscale structural disorder in manganese oxide particles embedded in Nafion

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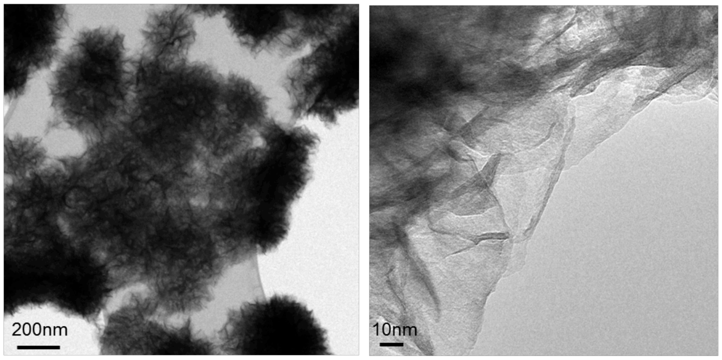
Contents:

Materials and synthesis: All chemicals and solvents were purchased from Sigma Aldrich and used as received. Nafion was purchased from Sigma in the form of acidic polymer dispersion, 117 Nafion, 5% solution in alcohol. Millipore water was used throughout to prepare the electrolyte solution. The manganese precursors, $[(Me_3TACN)_2Mn_2^{III}(\mu\text{-}O)(\mu\text{-}CH_3COO)_2](ClO_4)_2$ where Me_3TACN is N,N',N"-trimethyl-1,4,7-triazacyclononane, was prepared according to the reported procedures in the literature[1]. Reference Na-birnessite was synthesised by mixing 0.1M Mn^{2+} with 0.7M NaClO. The resulting precipitate was isolated by centrifuged and washing with water. The dehydrated form was prepared by an additional acetone wash and drying at 60°C in an oven for 30 minutes.

TEM specimen preparation procedures of manganese oxides in Nafion: In order to avoid damage of Nafion modified electrodes during TEM specimen preparation, the materials were prepared directly on the carbon film coated TEM gold grids. The Nafion film was deposited on the grids by drop-casting 2 μL of the 5% Nafion suspension that has been diluted with ethanol. The films were firstly dried at room temperature and then heated in oven at 120 °C for 20 minutes. Doping was achieved by immersing the Nafion films coated TEM grids in 2mM acetonitrile solutions of Mn precursor complex for 10 minutes. The grids were then rinsed and dried at room temperature for 20 minutes. The application of potential was carried out directly on the Nafion modified TEM grids (as electrode) by transferring the doped Nafion film coated grids to a 0.10M Na_2SO_4 aqueous solution and applying a potential of 1.1 V vs. Ag/AgCl for 5 minutes, as used in electrochemistry experiments reported previously[2].

Fig. S1 shows TEM images of the manganese oxide particles formed from electro-oxidation (*not in Nafion*), and the synthetic Na-birnessite particles, in comparison with the manganese oxide particles in Nafion, as shown in Fig. 1. It can be seen that the electro-oxidised particles form large size of clusters (order of 100nm) with needle-like morphologies (Fig. S1(a)). This morphology is distinctly different from the synthetic Na-birnessite (Fig. S1(b)). HRTEM image of the electro-oxidised particles (Fig. S1(a)right) shows sheet-like textures, and the edge of the sheets rolled into tubes, giving the needle like cluster morphologies shown in the lower magnification image. The particle morphologies and distributions of both electro-oxidised particles and synthetic Na-birnessites are different from the manganese oxides particles in Nafion, which show good dispersion through out the Nafion film and the sizes of the particles are smaller (10nm).

(a) Electro-oxidised manganese oxide (not in Nafion)



(b) Synthetic Na-birnessite

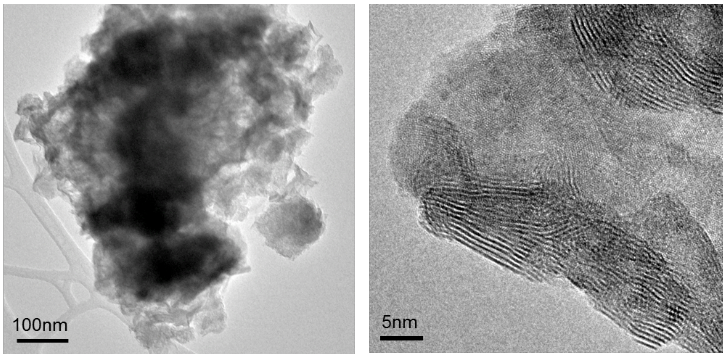


Figure S1: TEM images of the manganese oxide particles. (a) Manganese oxide particles formed from electro-oxidation of Mn^{II} precursors. (b) Synthetic Na-birnessite particles.

Catalytic activity testing Photo-electrochemical (PEC) testing has been performed to access the catalytic activities. Inductively coupled plasma-mass spectrometry (ICP-MS) has also been carried out to measure the composition in order to determine the normalised (per Mn) activity. The PEC measurements were performed at a constant potential 1.0V (vs Ag/AgCl), 0.10M Na_2SO_4 ($pH = 6.5$) and a light intensity of $150 mW/cm^2$. For the loading of the Mn^{III} dimer precursors (0.7 μg per cm^2, measured using ICP-MS) area in Nafion of approximately 25 μL, the net photocurrent was measured to be 31 μA per cm^2. Controlled potential electrolysis (CPE) at either 1.2V or 1.4V vs NHE, a light intensity of $150 mW/cm^2$ and pH=6.5, together with the ICP-MS measurement, was used to determine the turnover frequency (TOF) per Mn center. The values was estimated to be 44 molecules of O_2 per Mn per hour, at 1.0V vs Ag/AgCl, overpotential = 350mV[2]. This is about one order of magnitude higher than the unsupported manganese oxide particles. For example, TOF for unsupported birnessite with various interlay cations is 0.2-1.1 at 1.4V vs NHE, pH=2[3].

(S)TEM imaging, electron diffraction and energy dispersive spectroscopy techniques Characterisation of the manganese oxide particles in Nafion has been carried out using a TEM (JEOL 2100F) operated at 200 kV. Annular-dark field (ADF) STEM, Bright-field (BF), high-resolution (HR) TEM imaging and selected area diffraction techniques as well as Energy dispersive X-ray spectroscopy (EDS) were used to elucidate the morphology, distribution and the structural changes of manganese oxide particles in Nafion. For the analysis of the coherent diffraction intensities (CDI), firstly, the camera length was calibrated using gold nanoparticles deposited on carbon films. The calibrated selected area diffraction patterns were then rotationally integrated to obtain one-dimensional diffraction intensity distributions. The background intensities in the 1-D diffraction intensity distributions were then subtracted using a least-square fitting criteria with model intensities calculated using a electron multiple-scattering formula, based on the nominal composition of the specimen.

Coherent diffraction intensity of particles in Nafion before and after electro-oxidation Fig. S2 shows the CDI of the manganese oxide particles in the Nafion. For comparison, the manganese precursor doped Nafion film before electro-oxidation is also shown. Before oxidation, Fig. S2(a) shows that the image contrast of the doped Nafion film doped is uniform. Its corresponding coherent diffraction intensity (Fig. S2(c) blue line) shows only broad peaks that are characteristic of an amorphous material, suggesting that the manganese dimer precursors are well-dispersed in the Nafion film.

After applying an electric potential of 1.1 V (vs. Ag/AgCl), the coherent diffraction intensity in Fig. S2(c) shows three additional narrower peaks (red line labelled with arrows) superimposed on the broad peaks that closely resemble those of doped Nafion *before* applying potential. This observation is consistent with the formation of manganese oxide particles.

Comparisons of simulated electron diffraction pattern of various manganese oxide phases The CDI of the manganese oxide particles in Nafion has been compared to a series of manganese oxide crystals with Mn oxidation states between $\mathrm{Mn^{III}}$ and $\mathrm{Mn^{IV}}$. Figure S3 shows the simulated electron diffraction intensities of the series of manganese oxides, generated using atomic structures obtained from the ICSD database. These oxides

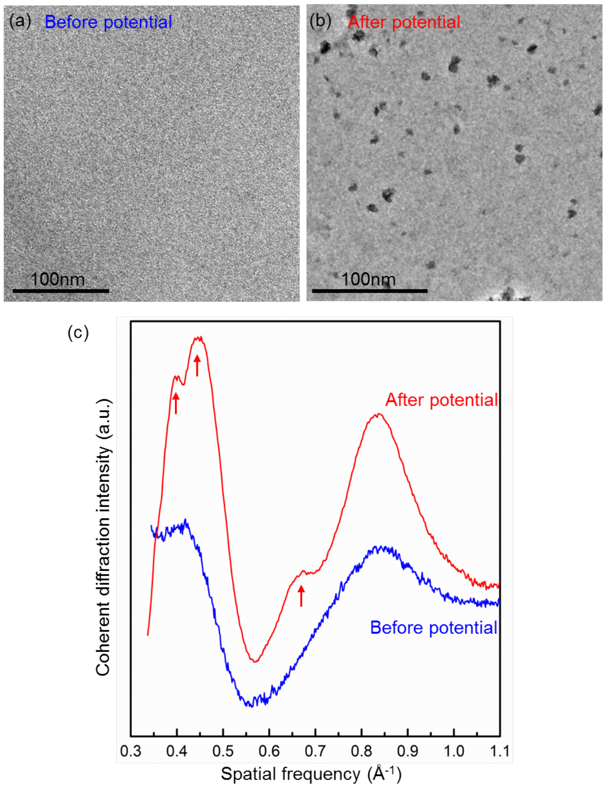


Figure S2: Bright-field TEM images of the manganese precursor doped Nafion film before electro-oxidation (a), manganese oxide particles formed in Nafion (b) after applying 1.1 V potential to (a) for 5 minutes and (c) their corresponding coherent diffraction intensities.

include both dehydrated[4] and hydrated monoclinic birnessite[5], pyrolusite[6], hollandite[7] and todorokite[8]. It can be seen that the CDI of the manganese oxide particles in Nafion (dotted line) is best matched with the dehydrated birnessite structure. Although hydrated birnessite also provides fairly good agreement, there are prominent peaks from hydrated birnessite at 0.53-0.56 Å^{-1} that are absent in the experimental data from the electro-oxidised product.

Electron scattering simulations of structural disorder in manganese oxide The electron powder diffraction intensities were simulated using the electron scattering factor by E. J. Kirkland[9]. The diffraction intensities were calculated based on the kinematical approximation, and the simulation parameters including electron wave length, camera length and the modulation transfer function of the camera correspond to the experimental conditions. The particle size effect was simulated using the Scherrer equation. The effect of Mn vacancies and layer mis-registration were calculated based on the modified atomic models of the perfect monoclinic birnessite phase. The Mn vacancies were

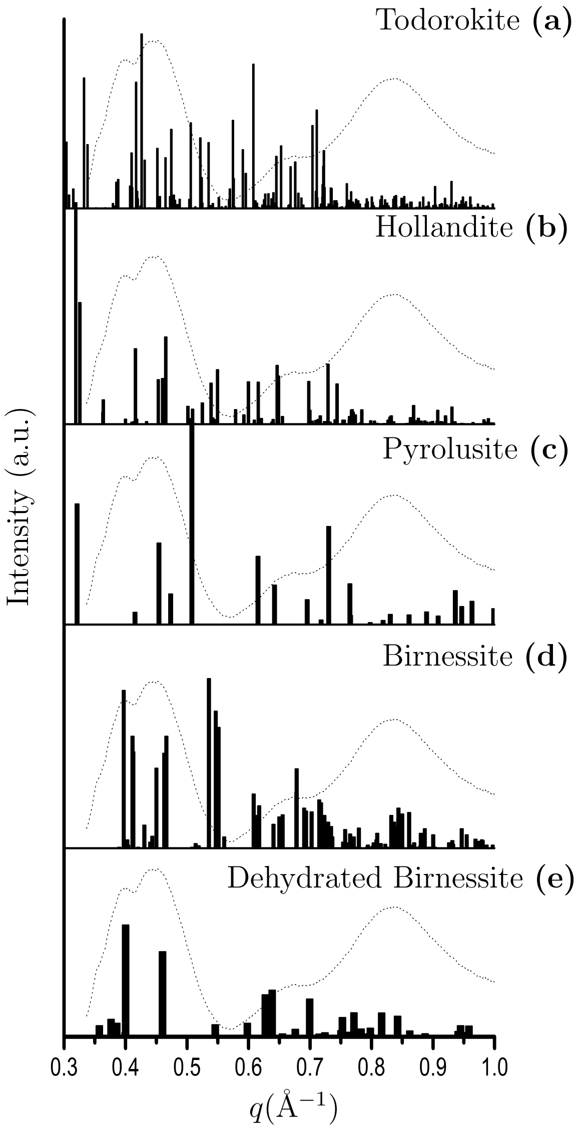


Figure S3: Comparison of the coherent diffraction intensity of the electro-oxidised product in Nafion (dotted line) and simulated results from a series of manganese oxides. (a) todorokite; (b) hollandite; (c) pyrolusite; (d) Na-birnessite (hydrated); (e) Na-birnessite (dehydrated).

modelled by randomly selecting 40% of Mn sites in a 5×5×5 supercell of the birnessite structure. The diffraction intensity was obtained by averaging over 10 configurations. The layer mis-registration was modelled by randomly shifting the Mn and Na positions along z-axis for the averaged magnitude of 0.1Å in a 5×5×5 supercell. The diffraction intensity was obtained, again, by averaging over 10 configurations.

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