

Supporting Information for

MnNiCoO₄/N-MWCNT Nanocomposite Catalysts with High Selectivity in Membraneless Direct Formate Fuel Cells and Bifunctional Activity for Oxygen Electrochemistry

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Experimental details

1. Synthesis of MnNiCoO₄/N-MWCNT and MnCo₂O₄/N-MWCNT catalysts:

Multiwall carbon nanotube (MWCNT) (US Research Nanomaterials, Inc.) powder was first pretreated (oxidized) by refluxing the MWCNT powder (0.2 g) in 50 mL of nitric acid at 80 °C for 4 h. Then the mixture was cooled to room temperature and diluted with 100 mL of de-ionized (DI) water. The resulting solid was collected by centrifugation, washed with DI water for several times, and dried at 50 °C under vacuum.

For a typical synthesis in this study, 0.51 mL of 0.6 M Mn(OAc)₂, 0.765 mL of 0.4 M Ni(OAc)₂, and 0.51 mL of 0.6 M Co(OAc)₂ aqueous solutions were added to a 30 mL ethanol solution with 0.1 g MWCNT suspension, followed by the addition of 2.5 mL of NH₄OH at RT, which was used to mediate the nucleation of the metal species and provide a source for nitrogen doping. The reaction was kept at 80 °C with stirring for 24 h. After that, the above reaction mixture was transferred to an 80 mL autoclave for hydrothermal reaction at 150 °C for 3 h to obtain N-doping and crystallization of the metal oxide nanoparticles on MWCNT. The resulting product was collected by centrifugation and washed with ethanol and water. The MnNiCoO₄/N-MWCNT composite product was ~ 170 mg after drying (~ 41.0 wt.% MnNiCoO₄). The MnCo₂O₄/N-MWCNT composite catalysts was synthesized with the same procedure as above but with appropriate amounts of Mn(OAc)₂ and Co(OAc)₂ precursors and MWCNT powder (molar ratio of Mn : Co = 1 : 2 with a target MnCo₂O₄ content of 42.0 wt.% on N-MWCNT).

2. Characterization:

Morphological characterization of the catalysts was carried out with a Hitachi S-5500 scanning transmission electron microscope (STEM). The elemental mapping results were obtained with an energy-dispersive spectrometer (EDS) attached to the Hitachi S-5500 STEM. The XRD data were collected on a Rigaku D/MAX-RC X-ray diffractometer equipped with Cu K α radiation between 10° and 80° in a step of 0.02°. The Raman spectra of the catalysts were collected with a Witec Alpha 300 micro-Raman confocal microscope. Transition-metal ratios in the sample were determined with a Varian 715-ES inductively coupled plasma–optical emission spectroscopy (ICP-OES) analyzer.

3. Electrochemical Measurements:

3.1. Cyclic Voltammetry (CV): 10 mg of the powder catalyst was dispersed into a solution comprising of 800 μ L DI water, 200 μ L isopropanol (IPA), and 18 μ L Nafion solution (15 wt.%) by sonication for 10 min to form a homogenous ink. Then 5 μ L of the catalyst ink was loaded onto a glassy carbon electrode of 5 mm in diameter. Cyclic voltammetry was conducted with an Autolab potentiostat (PGSTAT128N) in a three-electrode electrochemical cell using saturated calomel electrode (SCE) as the reference electrode, a Pt mesh as the counter electrode, and the sample modified glassy carbon electrode as the working electrode. 1.0 M KOH solution was used as the electrolyte, which was saturated with oxygen by bubbling O₂ prior to the start of each experiment. A flow of O₂ was maintained at a constant rate over the electrolyte during the recording of CV in order to ensure its continued O₂ saturation. CV profiles were recorded at a scan rate of 5 mV s⁻¹.

3.2. Rotating Disk Electrode (RDE) Measurement: The catalyst-modified working electrode was prepared by the same method as for CV. The working electrode was scanned cathodically at a rate of 5 mV s⁻¹ with varying rotating speed from 400 to 1600 rpm. Koutecky-Levich plots (J^{-1} vs. $\omega^{-1/2}$) were analyzed with various electrode potentials. The slopes of their best linear fit lines were used to calculate the number of electrons transferred (n) on the basis of the Koutecky-Levich equations:

$$\frac{1}{J} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}$$
$$B = 0.62nFC_0D_0^{2/3}v^{-1/6}; J_K = nFkC_0$$

where J is the measured current density, J_K is the kinetic current density, ω is the angular velocity, n is transferred electron number, F is the Faraday constant, C_0 is the bulk concentration of O_2 , ν is the kinematic viscosity of the electrolyte, and k is the electron-transfer rate constant.

3.3. Rotating Ring–Disk Electrode (RRDE) Measurement: For the RRDE measurements, catalyst inks and electrodes were prepared by the same method as those for the RDE experiments. The disc electrode was scanned cathodically at a rate of 5 mV s⁻¹, and the ring potential was constant at 1.3 V vs. RHE. The % HO₂⁻ and the electron transfer number (n) were determined by the equations below:

$$HO_2^- = 200 \frac{I_r/N}{I_d + I_r/N}$$

$$n = 4 \frac{I_d}{I_d + I_r/N}$$

where I_d is disc current, I_r is ring current, and N is current collection efficiency of the Pt ring. N was determined to be 0.38 from the reduction of K₃Fe[CN]₆.

3.4. Oxygen Electrode Activities on Carbon-fiber Paper: For measurements on carbon-fiber paper, the working electrode was prepared by the deposition of 0.5 mg of catalyst onto 1 cm² carbon-fiber paper (Toray paper 090, Fuel Cell Store) from the catalyst inks prepared as those for the CV, RDE, and RRDE experiments. The cathodic linear sweep voltammetry profiles (for ORR measurement) were recorded in 1 M KOH solution with a constant flow of oxygen from 0 to -0.4 V vs. SCE at a scan rate of 5 mV s⁻¹. To obtain OER activities in 1 M KOH, the working electrode was scanned from 0 to 0.6 V vs. SCE.

3.5. Fuel cell performance testing: An in-house designed membraneless alkaline direct formate fuel cell (DFFC) with 5.0 cm² active area was used for cell performance test. Details of this cell can be found in our recent publication.¹ In this cell, Pd/C and MnCo₂O₄/N-MWCNT were, respectively, used as the anode and cathode catalysts. An aqueous solution comprising HCOOK as fuel and KOH as supporting electrolyte was fed as an anolyte through a chamber between the anode and the cathode catalyst layers. The operation of the membraneless alkaline DFFC was controlled with a fuel cell test station (850E, Scribner Associates Inc.). In traditional alkaline liquid-fed fuel cells, an alkaline anion-exchange membrane is required to provide a conductive path for the OH⁻ ion migration and to prevent the crossover of the liquid fuel and the oxidants. In the membraneless alkaline DFFC, the supporting electrolyte KOH sustains the migration of

OH⁻ ions. Since the cathode catalyst MnCo₂O₄/N-MWCNT does not catalyze the anode reaction, oxidation of the fuel will not take place at the cathode. In addition, extremely low solubility and diffusivity of O₂ in an aqueous alkaline solution suggests that the crossover of the cathode oxidant is not an issue either. Therefore, the anion-exchange membrane used in the traditional alkaline DLFCs can be excluded.

1. X. Yu and A. Manthiram, *Appl. Catal. B-Environ.*, 2014, **165**, 63-67.

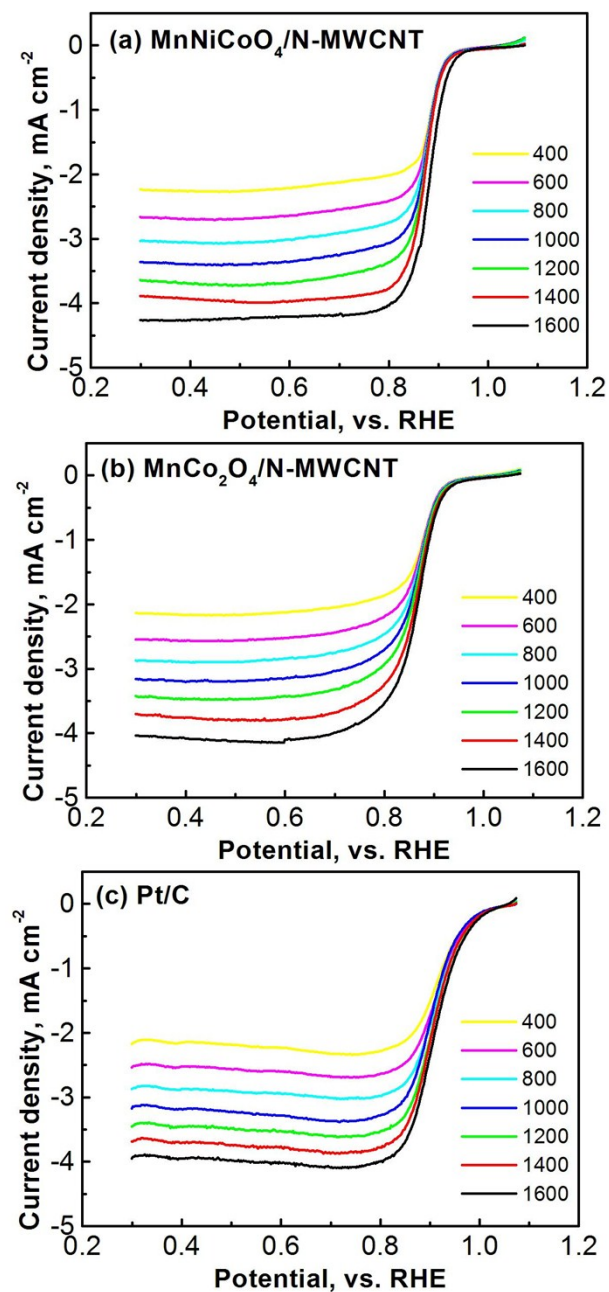


Figure S1. Rotating-disk electrode (RDE) voltammograms of the (a) $\text{MnNiCoO}_4/\text{N-MWCNT}$, (b) $\text{MnCo}_2\text{O}_4/\text{N-MWCNT}$, and (c) Pt/C (c) catalysts in O_2 -saturated 1 M KOH with a sweep rate of 5 mV/s at various rpm.

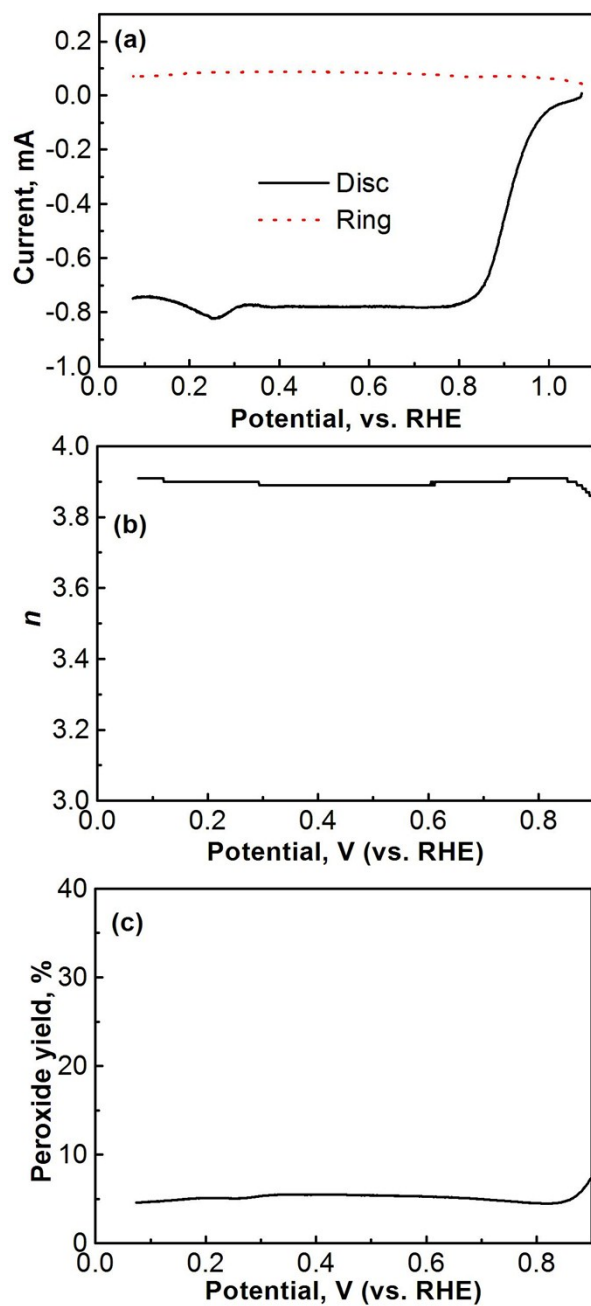


Figure S2. (a) Rotating ring-disk electrode (RRDE) voltammograms of the Pt/C catalyst in O₂-saturated 1 M KOH at 1600 rpm. The disk potential was scanned at 5 mV s⁻¹ and the ring potential was constant at 1.3 V vs. RHE. (b) The electron transfer number n and (c) the percentage of peroxide with respect to the total oxygen reduction products of the Pt/C catalyst at various potentials based on the corresponding RRDE results.

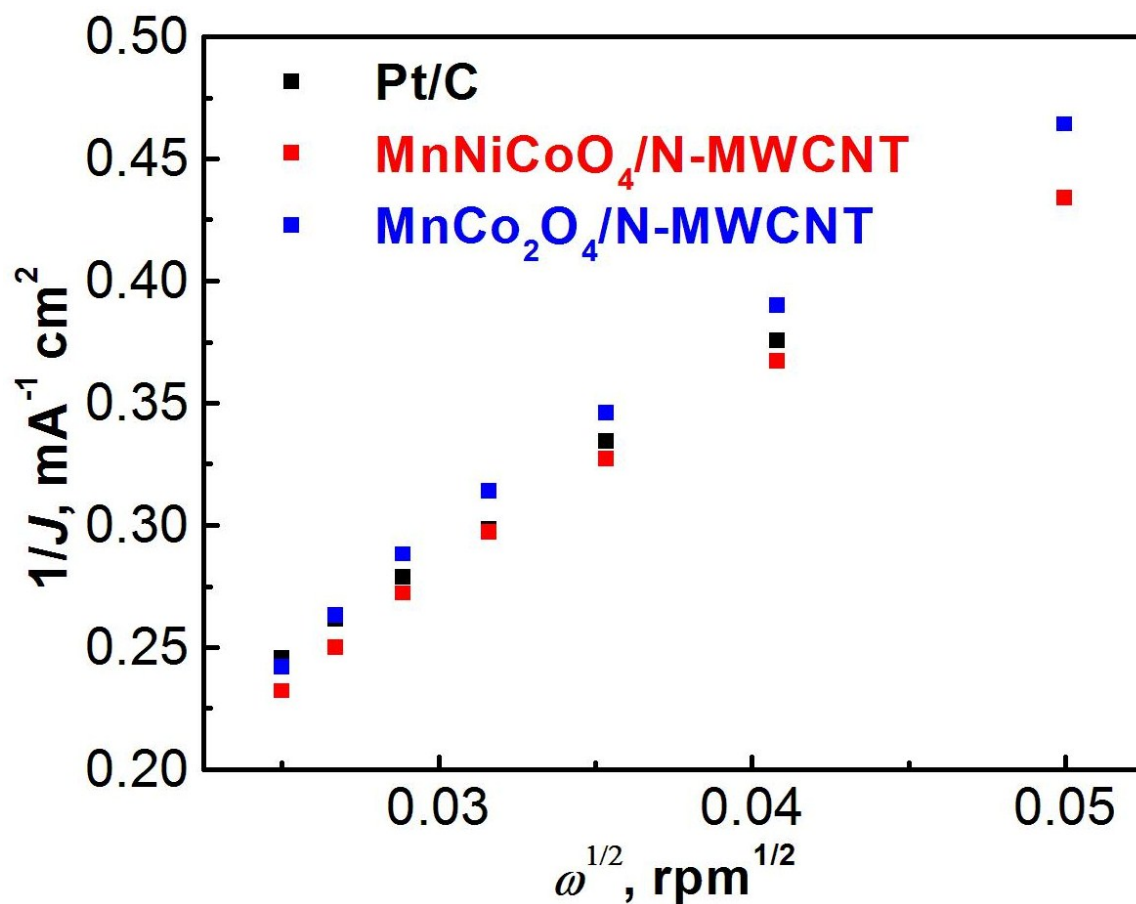


Figure S3. Koutecky–Levich plots for ORR in O₂-saturated 1.0 M KOH on the MnNiCoO₄/N-MWCNT, MnCo₂O₄/N-MWCNT, and Pt/C catalysts. The data were derived from RDE experiments shown in Figure S1.