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A nanocomposite electrocatalyst consisting of MnNiCoO_4 nanoparticles on nitrogen-doped multi-wall carbon nanotubes has been synthesized. In alkaline media, this catalyst exhibits high activity for oxygen reduction and evolution reactions, but no activity for formate oxidation. A membraneless alkaline direct formate fuel cell system is demonstrated based on this catalytic selectivity.

Oxygen electrochemistry including both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is of significant focus currently for a variety of renewable energy storage/generation applications such as metal–air batteries and fuel cells.¹ Platinum-based materials are known to be the most active catalysts for ORR in both acidic and alkaline media, but their application is hampered by the limited abundance and high cost of Pt.² Compared with its behavior in acidic medium, ORR in alkaline medium is more facile and can be catalyzed by a broader range of materials.³ Metal oxides and doped carbon materials have recently been widely investigated as ORR catalysts in alkaline solutions.⁴ However, oxides and carbon materials usually exhibit much lower mass activity compared to Pt-based catalysts.

Recently, hybrid ORR catalysts based on transition-metal oxides deposited onto carbon nanotubes or graphene matrices have been shown to exhibit high mass activity for ORR.⁵ For example, oxides such as Co_3O_4 and MnCo_2O_4 deposited onto nitrogen-doped graphene have shown high activity and stability for ORR.⁵ We recently reported a membraneless alkaline direct formate fuel cell (DFFC) developed using a

$\text{MnNiCoO}_4/\text{N-MWCNT}$ nanocomposite catalyst with high selectivity in membraneless direct formate fuel cells and bifunctional activity for oxygen electrochemistry†

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catalyst-selective strategy, which was inspired by an experimental observation that a highly ORR active cathode catalyst (Pt) showed almost no catalytic activity for formate oxidation reaction (FOR).⁶ We show here that MnNiCoO_4 nanoparticles deposited onto nitrogen-doped carbon nanotubes ($\text{MnNiCoO}_4/\text{N-MWCNT}$) exhibit even better catalytic selectivity (high ORR activity but FOR inactivity) than Pt, demonstrating it as an excellent cathode catalyst for the membraneless DFFC system. In addition, we show that the $\text{MnNiCoO}_4/\text{N-MWCNT}$ nanocomposite exhibits high OER activity as well, demonstrating the bifunctional activity necessary for rechargeable metal–air batteries.

The $\text{MnNiCoO}_4/\text{N-MWCNT}$ nanocomposite catalyst was synthesized by impregnation–hydrothermal processes. The synthesis details are provided in the ESI.† For comparison, a binary metal oxide catalyst composed of $\text{MnCo}_2\text{O}_4/\text{N-MWCNT}$ was also synthesized using the same method. The scanning transmission electron microscopy (STEM) image of the synthesized $\text{MnNiCoO}_4/\text{N-MWCNT}$ catalyst displayed in Fig. 1a clearly reveals the formation of nanocrystals with a particle size of ~5 nm on the MWCNT support. Energy dispersive spectroscopy (EDS) analysis (Fig. 1b) indicates that the molar ratio of Mn:Co:Ni in the catalyst is 36:34:30, while inductively coupled plasma (ICP) analysis reveals this ratio in the catalyst to be 34.5:33.6:31.9, which is close to the ratio of the Mn, Co, and Ni precursors used in the synthesis (Mn:Co:Ni = 1:1:1). The MnNiCoO_4 loading on the MWCNT was ~41.2 wt.% (the target loading was 42.0 wt.%) as determined by the weight gain of the MWCNT after the deposition of MnNiCoO_4 . The X-ray diffraction (XRD) pattern of the $\text{MnNiCoO}_4/\text{N-MWCNT}$ catalyst (Fig. 1c) shows that the synthesized nanocrystals are single-phase with a cubic spinel structure (XRD pattern of the nitrogen doped MWCNT is also shown here for comparison). The Raman spectra of the $\text{MnNiCoO}_4/\text{N-MWCNT}$ and $\text{MnCo}_2\text{O}_4/\text{N-MWCNT}$ catalysts displayed in Fig. 1d show wider (higher width-to-height ratio after normalization) peaks for both the D and G bands in comparison with those of the pristine MWCNT, but there is

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† Electronic supplementary information (ESI) available: Full experimental details, rotating-disc electrode (RDE) voltammograms of the Pt/C, $\text{MnNiCoO}_4/\text{N-MWCNT}$, and $\text{MnCo}_2\text{O}_4/\text{N-MWCNT}$ catalysts at various rotating speeds, Koutecky–Levich plots derived from the RDE voltammograms, rotating ring-disc electrode (RRDE) voltammograms of the Pt/C catalyst, and the electron transfer number n and the percentage of peroxide with respect to the total oxygen reduction products of the Pt/C catalyst. See DOI: 10.1039/c4cy01702a

Fig. 1 (a) STEM image and (b) EDS spectrum of the MnNiCoO₄/N-MWCNT catalyst. (c) XRD patterns of the MnNiCoO₄/N-MWCNT and MnCo₂O₄/N-MWCNT catalysts. (d) Raman spectra of the MnNiCoO₄/N-MWCNT (black) catalyst and pristine MWCNT (blue).

no shift in the peak position. The above phenomena reveal a clear nitrogen-doping characteristic according to a previous study.⁷

The electrocatalytic activity of the MnNiCoO₄/N-MWCNT catalyst for ORR was first characterized by cyclic voltammetry (CV) in 1 M KOH on a glassy carbon electrode and compared with that of the MnCo₂O₄/N-MWCNT and Pt/C catalysts (Fig. 2a). The ORR onset potential and peak potential of the MnNiCoO₄/N-MWCNT catalyst are, respectively, ~0.95 and ~0.88 V *versus* the reversible hydrogen electrode (RHE), which are ~20 mV more negative than that of the Pt/C catalyst, but ~10 mV more positive than that of the MnCo₂O₄/N-MWCNT catalyst. It has been reported that Mn substitution in a Co₃O₄/graphene hybrid catalyst to give MnCo₂O₄/graphene enhances the ORR activity.^{5b} The MnNiCoO₄ catalyst presented here further improves the ORR activity compared to MnCo₂O₄. The representative rotating-disc electrode (RDE) characteristics (linear sweep voltammograms at a rotating rate of 1600 rpm) of the catalysts in 1 M KOH solution saturated with oxygen are compared in Fig. 2b (the detailed RDE profiles at different rotating speeds are provided in Fig. S1†). The MnNiCoO₄/N-MWCNT catalyst also shows superior ORR performance to MnCo₂O₄/N-MWCNT in terms of disk current density and half-wave potential. In addition, MnNiCoO₄/N-MWCNT shows a half-wave potential similar to Pt/C (only ~20 mV difference).

The oxygen reduction reaction pathway on the catalysts was studied with a rotating ring-disk electrode (RRDE). Fig. 2c displays the voltammetry profiles of the disk and ring recorded at 1600 rpm in 1 M KOH saturated with O₂ for the MnNiCoO₄/N-MWCNT and MnCo₂O₄/N-MWCNT catalysts. MnNiCoO₄/N-MWCNT shows a higher disk current (O₂ reduction) and a relatively smaller ring current (peroxide oxidation) than MnCo₂O₄/N-MWCNT (inset in Fig. 2c). The electron

Fig. 2 (a) Cyclic voltammetry (CV) profiles of the Pt/C, MnNiCoO₄/N-MWCNT, and MnCo₂O₄/N-MWCNT catalysts on glassy carbon electrodes in O₂-saturated 1 M KOH. (b) Rotating-disk electrode voltammograms of Pt/C, MnNiCoO₄/N-MWCNT, and MnCo₂O₄/N-MWCNT catalysts in O₂-saturated 1 M KOH at a scan rate of 5 mV s⁻¹ at 1600 rpm. (c) Rotating ring-disk electrode voltammograms of the MnNiCoO₄/N-MWCNT and MnCo₂O₄/N-MWCNT catalysts 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. The inset shows the magnified ring currents. (d) The electron transfer number *n* and (e) percentage of peroxide with respect to the total oxygen reduction products of the MnNiCoO₄/N-MWCNT and MnCo₂O₄/N-MWCNT catalysts at various potentials based on the corresponding RRDE results. (f) Oxygen reduction polarization curves of the Pt/C, MnNiCoO₄/N-MWCNT, and MnCo₂O₄/N-MWCNT catalysts loaded onto carbon-fiber papers in 1 M KOH electrolyte saturated with oxygen. (g) Oxygen evolution currents of Pt/C, MnNiCoO₄/N-MWCNT, and MnCo₂O₄/N-MWCNT catalysts loaded onto carbon-fiber paper in 1 M KOH electrolyte.

number for oxygen reduction (*n*) and the percentage of peroxide species relative to the total oxygen reduction products calculated from the RRDE curves in Fig. 2c are provided, respectively, in Fig. 2d and e. The peroxide species is ~14% over the measured potential range for the MnNiCoO₄/N-MWCNT catalyst, which is lower than that found for MnCo₂O₄/N-MWCNT (~16%). The average electron transfer number approaches 3.8 for the MnNiCoO₄/N-MWCNT catalyst, which is very close to that of the Pt/C catalyst (Fig. S2†). In contrast, the electron transfer number is ~3.7 for MnCo₂O₄/N-MWCNT within the potential frame of 0.3–0.9 V vs. RHE. The above results indicate that the ORR catalyzed by either the MnNiCoO₄/N-MWCNT or MnCo₂O₄/N-MWCNT catalyst occurred mainly through a four electron pathway, which is in agreement with the RDE analysis results (Fig. S3†).

In order to investigate the electrochemical performance of the catalysts under conditions close to those present in

alkaline fuel cells or metal–air batteries, experiments were performed with the samples prepared by loading the catalysts onto carbon paper. The cathodic polarization curves of the $\text{MnNiCoO}_4/\text{N-MWCNT}$ and $\text{MnCo}_2\text{O}_4/\text{N-MWCNT}$ catalysts are presented in Fig. 2f and compared with that of the commercial Pt/C catalyst. The current density generated with $\text{MnNiCoO}_4/\text{N-MWCNT}$ is higher than that with $\text{MnCo}_2\text{O}_4/\text{N-MWCNT}$, which is consistent with the CV, RDE, and RRDE results. Interestingly, the current density of $\text{MnNiCoO}_4/\text{N-MWCNT}$ is lower than that of the Pt/C catalyst at low overpotentials but exceeded that of Pt/C at higher overpotentials. Fig. 2g compares the oxygen evolution reaction (OER) performance of the catalysts. With the substitution of Ni, the $\text{MnNiCoO}_4/\text{N-MWCNT}$ catalyst shows OER performance quite similar to that of $\text{MnCo}_2\text{O}_4/\text{N-MWCNT}$. But both of them show significantly higher OER catalytic activity than Pt/C, suggesting that the $\text{MnNiCoO}_4/\text{N-MWCNT}$ and $\text{MnCo}_2\text{O}_4/\text{N-MWCNT}$ composites are efficient bifunctional catalysts for ORR and OER.

The relevant mechanisms regarding the ORR enhancement of hybrid catalyst systems with strongly coupled transition-metal oxides and nitrogen-doped carbon materials have been previously studied with advanced material characterization techniques.⁵ The higher activity of the $\text{MnCo}_2\text{O}_4/\text{graphene}$ system relative to the $\text{Co}_3\text{O}_4/\text{r-GO}$ system has been attributed to Mn-doping.^{5b} The present study with $\text{MnNiCoO}_4/\text{N-MWCNT}$ reveals further benefits relative to $\text{MnCo}_2\text{O}_4/\text{N-MWCNT}$. Fig. 2a reveals that $\text{MnNiCoO}_4/\text{N-MWCNT}$ exhibits a significantly larger loop compared to $\text{MnCo}_2\text{O}_4/\text{N-MWCNT}$ in the CV profile, suggesting that Ni doping increases the electrochemically active surface area (or site) of the catalyst. The increased active sites and higher electrochemically active surface area are the likely factors for the enhancement in the catalytic activity of the $\text{MnNiCoO}_4/\text{N-MWCNT}$ system. A detailed mechanistic study of Ni-substitution will be performed in the future.

The practical performance of the $\text{MnNiCoO}_4/\text{N-MWCNT}$ catalyst was studied with our recently proposed membraneless alkaline direct formate fuel cell (DFFC), in which a highly selective cathode catalyst was required to avoid an anode reaction at the cathode.⁶ The FOR activity of the $\text{MnNiCoO}_4/\text{N-MWCNT}$ catalyst was tested and compared with that of the Pt/C catalyst in 1 M HCOOK solution with 1 M KOH as a supporting electrolyte. CV profiles are presented in Fig. 3a. A highly FOR active Pd/C catalyst is also shown here for comparison. Particularly, it is interesting to see that $\text{MnNiCoO}_4/\text{N-MWCNT}$ shows even lower activity than Pt/C for FOR. High activity for ORR and extreme inactivity for FOR suggest that $\text{MnNiCoO}_4/\text{N-MWCNT}$ is an excellent cathode catalyst for membraneless alkaline DFFCs.

The performance of the membraneless DFFCs with Pd/C as the anode catalyst and $\text{MnNiCoO}_4/\text{N-MWCNT}$ as the cathode catalyst was evaluated by operating a cell with 5 cm² active electrodes (areas of the anode and the cathode are identical) and a 2 mm thick flow chamber. The details regarding the principles and configuration of the membraneless

Fig. 3 (a) Cyclic voltammograms of the $\text{MnNiCoO}_4/\text{N-MWCNT}$, Pt/C, and Pd/C electrodes in an electrolyte containing 1.0 M HCOOK in 1.0 M KOH at 10 mV s⁻¹. Experiments were performed at ambient temperature. (b) Polarization curves and (c) power plots of the membraneless alkaline direct formate fuel cells (DFFCs) with Pd/C as the anode catalyst and $\text{MnNiCoO}_4/\text{N-MWCNT}$ or Pt/C as the cathode catalyst. The cells were operated at 25 °C and 50 °C.

DFFC are available in our previous publication.⁶ For single cell measurements, an anolyte solution containing 2.0 M HCOOK in 2.0 M KOH was pumped through the flow chamber at a flow rate of 0.5 mL min⁻¹. Oxygen was fed to the cathode at a flow rate of 100 mL min⁻¹ without back pressure. The Pd loading at the anode and the $\text{MnNiCoO}_4/\text{N-MWCNT}$ or Pt/C loading at the cathode were both 1.0 mg cm⁻². Cell performance was tested at 25 and 50 °C. Fig. 3b and c show the polarization curves and the corresponding power plots, respectively.

The open-circuit voltage (OCV) of the membraneless DFFC is ca. 1.05 V, a value which is higher than those of other direct liquid fuel cells (DLFCs) such as direct methanol fuel cells (DMFC), direct ethanol fuel cells (DEFC), and direct formic acid fuel cells (DFAFC).⁸ Under the testing conditions with low catalyst loading demonstrated in this study at 50 °C, the specific power of the membraneless DFFC is ca. 90 mW cm⁻² and the specific current at 0.6 V is ca. 120 mA cm⁻². This performance is comparable to that of alkaline DLFCs with alkaline anion-exchange membranes and with a high-loading Pt cathode catalyst.⁹ It is exciting to see that the cell with the $\text{MnNiCoO}_4/\text{N-MWCNT}$ cathode outputs higher power than that with the Pt/C cathode, especially at elevated temperatures (50 °C). As seen in Fig. 3a, the Pt/C catalyst shows slight catalytic activity for FOR, which may induce a certain level of mixed current during operation of membraneless DFFCs. On the other hand, $\text{MnNiCoO}_4/\text{N-MWCNT}$ does not show any positive current in the voltammetry profile within the potential domain of -0.7–0 V vs. SHE (DFFC operation potential frame), indicating a more selective sensitivity and the superiority of $\text{MnNiCoO}_4/\text{N-MWCNT}$ relative to Pt/C for operation of membraneless DFFCs.

In summary, we presented a nanocomposite catalyst consisting of MnNiCoO_4 nanoparticles on nitrogen-doped multi-wall carbon nanotubes (N-MWCNT) for ORR and OER. The $\text{MnNiCoO}_4/\text{N-MWCNT}$ catalyst exhibits excellent bifunctional catalytic activity (ORR and OER) for rechargeable alkaline metal–air batteries and high catalytic selectivity with high ORR activity but FOR inactivity in membraneless DFFCs, demonstrating superiority to Pt/C cathode catalysts.

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