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Manganese Cobalt Oxide Decorated Reduced Graphene Oxide as Multifunctional Material for Mechanically Rechargeable and Hybrid Zinc Air Batteries

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Spinel MnCo_2O_4 nanoparticles on nitrogen doped reduced graphene oxide ($\text{MnCo}_2\text{O}_4/\text{NGr}$) are synthesized for advanced zinc air batteries with remarkable cyclic efficiency and stability.

The synthesized $\text{MnCo}_2\text{O}_4/\text{NGr}$ exhibits ORR activity with a half-wave potential $E_{1/2}$ of 0.85 V (vs. RHE), comparable to the commercial Pt/C with $E_{1/2}$ of 0.88 V (vs. RHE) along with superior oxygen electrode activity $\Delta E = 0.91$ V for ORR/OER in alkaline media. Short and long term durability tests show that $\text{MnCo}_2\text{O}_4/\text{NGr}$ is more stable than Pt/C in alkaline environment. When deployed in a mechanically rechargeable zinc-air system, the $\text{MnCo}_2\text{O}_4/\text{NGr}$ functions with a stable discharge profile of 1.2 V at $20 \text{ mA}\cdot\text{cm}^{-2}$, a large discharge capacity of $707 \text{ mAh}\cdot\text{g}^{-1}_{\text{Zn}}$ at $40 \text{ mA}\cdot\text{cm}^{-2}$ and a high energy density of $813 \text{ Wh}\cdot\text{Kg}^{-1}_{\text{Zn}}$ under ambient air. Electrically rechargeable $\text{MnCo}_2\text{O}_4/\text{NGr}$ zinc-air battery displays hybrid behavior with both faradaic and oxygen redox charge-discharge characteristics, operating at higher voltage and providing higher power density and excellent cyclic efficiency of 86% for over 100 cycles compared to Pt/C with efficiency of around 60%. Hybrid zinc air

battery operates with a stable and energy efficient profile with low charge-discharge gap at current densities of 1, 5 and 10 mA.cm⁻².

1. Introduction

The harmful effects of fossil fuel based energy systems on the environment along with their sustainability concerns have provided the impetus for research on advanced energy conversion and storage systems. Multifunctional energy storage materials and devices are a subject of great interest as they can meet the global demand of clean and sustainable energy.^[1]

Metal-air batteries (M= Li, Zn, Al etc.) are the epitomes of these systems with the Li-air battery having the highest energy density.^[2] Although Li-air battery has the highest theoretical energy density, the commercialization of Li-air system faces numerous safety and stability issues due to highly reactive nature of lithium.^[3] Zn-air battery is especially attractive for commercialization point of view because of its high energy density, non-toxicity and abundance of Zn in the earth's crust.^[4] The theoretical energy density of Zn-air battery is about 4 times higher than the Li-ion battery. The commercialization of secondary Zn-air battery is impeded because of high catalyst cost, poor stability and low power density along with issues such as dendrite formation during recharge cycle, formation of ZnO on anode and electrolyte leakage.^[5] The mechanically rechargeable system alleviates the issue of Zn-dendrite formation by simple replacement of the Zn anode after each discharge cycle. By continuously replacing the metallic anode after each discharge, the Zn-air battery is stable for operation repeatedly. However, mechanical rechargeable systems also faces issues like i) high cost of expensive commercial Pt/catalyst used for ORR along with ii) poor durability owing to the instability of Pt/C over period of time in alkaline media which leads to gradual decay of the battery performance.^[6]

Transition metal oxides decorated on carbon nanomaterials have been reported as bifunctional electrocatalysts in alkaline environment.^[7] The strategy of introducing metal oxide nanoparticles (NPs) onto conductive carbon framework alleviates the problem of poor

1 conductivity which is associated with most of metal oxide NPs due to their low d-band
2 mobility.^[8] Oxides of cobalt are of especial interest because of their inherent high OER
3 activity. In Co_3O_4 , the mix valence of Co^{+2} and Co^{+3} in the spinel structure is reported to play
4 a vital role during ORR.^[9] A further improvement towards catalytic activity in the cobalt
5 oxide spinel is reported by the introduction of mix valence states of Mn^{+3} and Mn^{+4} into the
6 structure by doping with manganese. The introduction of manganese improves the M-O-C and
7 M-N-C bonding along with an increase in the catalytically active surface area.^[10] Liang *et al.*
8 developed manganese-cobalt oxides on N-doped reduced graphene oxide ($\text{MnCo}_2\text{O}_4/\text{N}$ -
9 rmGO) for ORR in alkaline media by solvothermal treatment of metallic salts with ammonia
10 solution in ethanol.^[10] The $\text{MnCo}_2\text{O}_4/\text{N}$ -rmGO was reported to have a better catalytic activity
11 for ORR than $\text{Co}_3\text{O}_4/\text{N}$ -rmGO hybrid but the OER activity of $\text{MnCo}_2\text{O}_4/\text{N}$ -rmGO was found
12 to be lower than the $\text{Co}_3\text{O}_4/\text{N}$ -rmGO. Porous spinel microspheres of cobalt and manganese
13 mixed oxides ($\text{CoMn}_2\text{O}_4/\text{C}$ and $\text{Co}_2\text{MnO}_4/\text{C}$) as highly efficient multifunctional catalysts were
14 prepared by the thermal degradation of the respective carbonate precursors at 400 °C.^[11]
15 Tetragonal $\text{CoMn}_2\text{O}_4/\text{C}$ catalyst was observed to be more active for ORR whereas cubic
16 $\text{MnCo}_2\text{O}_4/\text{C}$ was more active for OER, however, the half-wave potential $E_{1/2}$ of $\text{CoMn}_2\text{O}_4/\text{C}$
17 was 90 mV lower than that of the commercial Pt/C catalyst. Similarly CoMn_2O_4 anchored
18 onto nitrogen doped reduced graphene (N-rGO) oxide was reported by hydrothermal method
19 for Zn-air battery.^[12] The half-wave potential $E_{1/2}$ of $\text{CoMn}_2\text{O}_4/\text{N}$ -rGO was 50 mV more
20 positive compared to $\text{CoMn}_2\text{O}_4/\text{rGO}$ and 60 mV more negative compared to the commercial
21 Pt/C, respectively. Also, nickel cobalt oxide supported on reduced graphene oxide nanosheets
22 $\text{NiCo}_2\text{O}_4/\text{rGO}$ hybrid was reported by a facile chemical route with catalytic activity
23 comparable to commercial Pt/C in terms of onset potential and current density.^[13] To further
24 improve the oxygen reduction property of the $\text{MnCo}_2\text{O}_4/\text{NGr}$, one way is to embed the oxides
25 or metal into graphene, another is to make the oxides or metal to form the nanoporous
26 structures.^[14] More recently, hybrid zinc air batteries employing transition metal oxide
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1 faradaic transitions have been reported to improve power density and stability of zinc air
2 battery. By growing NiCo_2O_4 nanowires onto carbon coated Ni-foam, a hybrid zinc air battery
3 with high working voltage and high power density has been reported.^[15] The faradaic redox
4 transitions i.e. $\text{M-O} \leftrightarrow \text{M-O-OH}$ of $\text{M}=\text{Ni,Co}$ induce hybrid charge-discharge behavior
5 enabling the battery to work at a higher voltage with high power density. Similarly a hybrid
6 zinc air battery with high power density and energy density was reported using NiO/Ni(OH)_2
7 as the active material.^[16] The combination of faradaic redox reactions of the active nickel
8 species along with conventional ORR/OER at cell level was ascribed as the reason behind the
9 high energy density and power density of the hybrid battery.
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11 Herein, we synthesize MnCo_2O_4 nanoparticles anchored onto nitrogen doped reduced
12 graphene oxide ($\text{MnCo}_2\text{O}_4/\text{NGr}$) by hydrothermal treatment and explore their electrocatalytic
13 activity for ORR/OER in alkaline media along with supercapacitive properties. Primary and
14 mechanically rechargeable Zn-air batteries were made to confirm the activity and stability for
15 ORR in a practical application. The batteries were observed to function with an activity
16 similar to commercial Pt/C along with much superior stability in ambient air. A negligible
17 loss in discharge potential was observed after several recharges in the mechanical
18 rechargeable Zn-air battery. $\text{MnCo}_2\text{O}_4/\text{NGr}$ electrocatalyst was also observed to be active for
19 OER. The ΔE value for the $\text{MnCo}_2\text{O}_4/\text{NGr}$ system was recorded to be 0.91 V which also
20 confirms its superior bifunctional (ORR/OER) activity. Hybrid zinc air battery data reveals
21 that the combination of supercapacitive and ORR/OER reactions enables the battery to
22 function at higher discharge voltage resulting in high power density, exceptional cyclic
23 efficiency and low charge-discharge potential gap at current densities of 1, 5 and 10 $\text{mA}\cdot\text{cm}^{-2}$.
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2. Results and Discussion

25 **Figure 1** shows the XRD patterns of the as synthesized catalysts. Complete formation of
26 spinel MnCo_2O_4 on graphene is confirmed by the presence of well-defined peaks at 2θ
27 values of 30.6° , 36.1° , 43.9° , 58.2° and 63.6° corresponding to the (220), (311), (400), (511)
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1 and (440) planes respectively according to the JCPDS PDF card # 23-1237. The peak present
2 in all the patterns at about 2θ value of 25° corresponds to the reduced graphene support used
3 for the decoration of metal oxide nanoparticles. In case of use of only cobalt acetate salt
4 during hydrothermal treatment, most of the precursor is converted to spinel Co_3O_4 as
5 confirmed by the peaks located at 31° , 36.8° , 59.3° and 65.2° which are ascribed to (220),
6 (311), (511) and (440) planes respectively. However apart from Co_3O_4 , diffraction peak from
7 cobalt hydroxide is also present which shows that during the hydrothermal synthesis mixture
8 of cobalt oxide/hydroxide have been formed on the surface of graphene. This is in agreement
9 with the hydrothermal synthesis of different cobalt oxides by Dong *et al.* which also report a
10 degree of different oxide formation from cobalt acetate during the hydrothermal process.^[17] In
11 case of Manganese acetate precursor, formation of spinel Mn_3O_4 on graphene was confirmed
12 with the presence of several Mn_3O_4 peaks attributed to JCPDS PDF card # 24-0734.
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14 The SEM of a graphene flake decorated with MnCo_2O_4 is shown as **Figure 2a**. Plenty of
15 MnCo_2O_4 nanoparticles are observed to be uniformly distributed on the graphene flakes. The
16 atomic ratio of Mn:Co was also estimated and found to be nearly 1:2 over a point (spectrum
17 1) and a region (spectrum 2) as shown in Figure S1 in Supporting Information. The atomic
18 ratio of Mn:Co is consistent with the molar ratios of metallic salt precursors i.e. 1:2 used for
19 the formation of spinel MnCo_2O_4 . Apart from the elements of spinel metal oxide, a few peaks
20 from the glass substrate used for SEM are also present at 1.75 and 3.5 keV respectively.
21 Figure 2 (b, c) show low magnification TEM of $\text{MnCo}_2\text{O}_4/\text{NGr}$ along with selected area
22 electron diffraction (SAED). The crystallinity of the sample is confirmed by the presence of
23 discernable rings. These rings are related to the diffraction of electrons from (220), (311),
24 (400), (511) and (440) planes of MnCo_2O_4 . The SAED data is in agreement with the XRD
25 results which also show formation of pure MnCo_2O_4 on graphene flakes with the absence of
26 impurities. The high density of (311) facets of MnCo_2O_4 in HRTEM is in consistency with the
27 XRD data which show a preferential diffraction from the (311) planes with interplanar
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spacing value of 0.25 nm (Figure 2d). Also lattice fringes from (400) with $d=0.21$ nm are also visible in HRTEM. Moreover the dispersion of MnCo_2O_4 nanoparticles is uniform and homogeneous on graphene sheets on both macro and micro levels as evident from the SEM and TEM (Figure S2 in Supporting Information). Elemental mapping of the sample reveals a uniform dispersion of constituent elements across the area of interest. The treatment of the GO with ammonia reduces the GO to reduced graphene oxide along with its nitrogenation as confirmed by presence of nitrogen in Figure S2. These N doped sites in graphene are reported to be the anchoring sites for the nucleation and growth of nanoparticles. The uniform incorporation of N into the graphene sheets is therefore pivotal for the subsequent uniform dispersion of the metal oxide nanoparticles.^[9] Moreover to look into the effect of morphology on the electrocatalytic performance, we also carried out SEM and TEM analysis on the reference samples (Figure S3 in Supporting Information). The uniform dispersion of both Co_xO_y and Mn_3O_4 on reduced graphene oxide sheets is clearly visible from the electron micrographs. Co_xO_y nanoparticles were observed to be aggregated into larger spherical nanoparticles with diameter of 100-200 nm. On the other hand Mn_3O_4 were observed to grow into nanoparticles of 25-100 nm across with a rich amount of planar smooth surfaces. Finally reduced graphene oxide sheets were observed to be wrinkled and free from any nanoparticles. X-ray photoelectron spectroscopy (XPS) was performed to analyze the surface composition of $\text{MnCo}_2\text{O}_4/\text{NGr}$ and NGr to reveal the surface nitrogen contents (Figure 3). $\text{MnCo}_2\text{O}_4/\text{NGr}$ survey reveals the presence of C, O, N, Co and Mn species. High resolution Co2p shows the peaks $2p_{1/2}$ and $2p_{3/2}$ with peak difference of 14.9 eV. The shoulders to the main peaks can be ascribed to the satellite peaks for cobalt. Similarly Mn2p high resolution XPS reveals the presence of $2p_{1/2}$ and $2p_{3/2}$ peaks at 641.8 eV and 652.3 eV respectively. For nitrogen doped carbons, quantity and type of N doping is crucial for electrocatalytic performance. Surface N contents for $\text{MnCo}_2\text{O}_4/\text{NGr}$ were measured to be 6.24%. High resolution N1s spectra revealed the presence of pyrolic, pyridinic and graphitic N-types in $\text{MnCo}_2\text{O}_4/\text{NGr}$ (Figure 3d).

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Pyrolic-N was observed to be 76.28%, pyridinic-N as 15.22% and graphitic-N was found to be 8.49% of the total N. Survey XPS spectrum of NGr shows the presence of only C,O and N (Figure 3e). The absence of metallic impurities confirms the purity of sample. The % N in NGr was measured to be 8.65 % i.e. about 2.5 % more than the MnCo₂O₄/NGr. High resolution N1s spectrum reveals the presence of pyrolic, pyridinic and graphitic N-types (Figure 3f). For NGr, Pyrolic-N was observed to be 71.79%, pyridinic-N as 16.3% and graphitic-N was found to be 11.9% of the total N. Compared to MnCo₂O₄/NGr, a higher graphitic, lower pyrolic and almost similar pyridinic content are observed in NGr. (Figure S4 in supporting information)

Catalyst inks for all the samples were made and deposited onto GCE for evaluation of their electrocatalytic performance for ORR in alkaline media. Cyclic Voltammograms (CV) in both N₂ and O₂ saturated 0.1 M KOH were recorded as shown in **Figure 4**. In case of O₂ saturated electrolytes, cathodic peak in the 0.8-0.9 V vs. RHE region is attributed to the reduction of molecular oxygen on the surface of the electrocatalysts. From these CVs, a discernable large ($j = 1.72 \text{ mA}\cdot\text{cm}^{-2}$) and most positive ($E = 0.85 \text{ V vs. RHE}$) reduction peak for molecular oxygen is observed for MnCo₂O₄/NGr compared to the rest, highlighting the superior activity of spinel MnCo₂O₄ for ORR in alkaline media. The order of catalytic activity for the catalysts based on CV measurements in O₂ saturated KOH solution is MnCo₂O₄/NGr > Co_xO_y/NGr > Mn₃O₄/NGr > NGr. The O₂ reduction peak is absent in N₂ saturated electrolytes as shown by the red dashed lines for each catalyst. Redox couples of both Mn⁺/Co⁺ are present in the N₂ saturated CV plot of MnCo₂O₄/NGr whereas only Co⁺ and Mn⁺ are observed for the N₂ saturated CV plots of Co_xO_y/NGr and Mn₃O₄/NGr respectively. This electrochemical data is in agreement with the structural characterization information of the aforementioned catalysts which indicates the formation of corresponding oxides without the presence of any impurities. For the Co_xO_y/NGr case, taking into account thermodynamic data provided by literature, faradaic phenomenon observed at lower potentials can be associated with Co²⁺/Co³⁺ redox

1 transition whereas the other found at higher potentials is attributed to $\text{Co}^{3+}/\text{Co}^{4+}$ redox
2 transition.^[18] In case of $\text{Mn}_3\text{O}_4/\text{NGr}$ two anodic peaks are related to the oxidation of $\text{Mn}(\text{OH})_2$
3 to Mn_3O_4 and Mn_3O_4 to MnOOH respectively, along with a broad cathodic peak as described
4 in literature.^[19] The CV curve for graphene treated with ammonia i.e. 'NGr' was observed to
5 be quasi-rectangular in shape along the current-potential axis, without any redox peaks. This
6 demonstrates absence of any Mn^+/Co^+ ions and excellent capacitance behavior with fast
7 diffusion of electrolyte ions over graphene surface.^[20]

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17 The ORR activity of the graphene supported electrocatalysts was further investigated by
18 linear scan voltammetry. LSV plots were obtained in O_2 saturated 0.1 M KOH at different
19 rotation rates of catalyst loaded GCE. **Figure 5a** shows the comparative LSVs of different
20 rotation rates of catalyst loaded GCE. **Figure 5a** shows the comparative LSVs of different
21 catalysts at 1600 rpm. The superior electrocatalytic activity of $\text{MnCo}_2\text{O}_4/\text{NGr}$ nanoparticles is
22 markedly evident from LSVs. The ORR is kinetically controlled over the surface of
23 $\text{MnCo}_2\text{O}_4/\text{NGr}$ in the potential range of 0.9-1.1 V vs. RHE, a mix of kinetic and diffusion
24 controlled in 0.8-0.9 V vs. RHE region and becomes diffusion limited from 0.8V vs. RHE
25 onwards. $\text{MnCo}_2\text{O}_4/\text{NGr}$ was observed to have an onset potential ' E_o ' of 0.93 V vs. RHE and
26 half wave potential of 0.85 V vs. RHE respectively. The half wave potential, an important
27 ORR parameter which describes the performance of catalyst under load, of $\text{MnCo}_2\text{O}_4/\text{NGr}$
28 was only 30mV more negative compared to commercial Pt/C which confirms the superior
29 activity of $\text{MnCo}_2\text{O}_4/\text{NGr}$. This important parameter was also better compared to other
30 recently reported metal oxide decorated carbon nanomaterials such as tetragonal $\text{CoMn}_2\text{O}_4/\text{C}$,
31 cubic $\text{MnCo}_2\text{O}_4/\text{C}$, cobalt ferrite oxide (CoFe_2O_4) nanospheres, $\text{Co}_3\text{O}_4/\text{Co}_2\text{MnO}_4$
32 nanocomposites, NiCo_2O_4 on N-doped graphene and surface tuned Co_3O_4 NPs on graphene.^{[9,}
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11, 21] Moreover from the TGA plot (Figure S5 in Supporting Information), MnCo_2O_4 loading
on nitrogenized graphene oxide was determined to be 52.57 %, which is 15 to 30% lower than
similar metal oxides on nitrogen doped reduced graphene electrocatalysts for ORR.^[7a, 9-10]
The thermo gravimetric analysis also revealed a small weight loss due to hydroxyl species at

1 lower temperature followed by a large weight lost at 300-450 °C due to burning of carbon
2 which is also manifested by the exothermic peak at the same temperatures in the DSC plot.
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4 The large ORR activity accompanied with a lower metal oxide loading endorses the superior
5 catalytic activity of MnCo₂O₄/NGr at a lower cost. Apart from having more positive onset
6 and half-wave potentials compared to the rest, MnCo₂O₄/NGr was observed to have the
7 largest value of limiting current density i.e. 5.12 mA.cm⁻². The enhanced activity for oxygen
8 reduction of MnCo₂O₄/NGr compared to the rest of the catalysts is in agreement with the CV
9 data which shows the most positive values of potential and largest current density for
10 reduction of molecular oxygen on the surface of MnCo₂O₄/NGr. The loading effect/content of
11 MnCo₂O₄ on NGr support on the electrocatalytic behavior of the MnCo₂O₄/NGr was also
12 examined (Figure S6 in Supporting Information). Both ORR and OER behavior of the
13 MnCo₂O₄/NGr composite were sensitive to the relative ratio of MnCo₂O₄ to NGr. Either too
14 high as in MnCo₂O₄/ 0.5 NGr or too low as in MnCo₂O₄/ 2 NGr, ratio of MnCo₂O₄ to NGr
15 was found to deteriorate the bifunctional catalytic activity of the MnCo₂O₄/NGr composite.
16 On the basis of the optimum MnCo₂O₄ to NGr ratio of nearly 1:1 (as measured from TGA),
17 we choose MnCo₂O₄/NGr for further RDE and battery performance evaluation, as this
18 composition would offer lowest overpotentials during oxygen reduction on battery discharge
19 and oxygen evolution on battery recharge. Furthermore, in order to ascertain the important
20 function of NGr in the MnCo₂O₄/NGr composite, we also performed ORR/OER analysis on
21 the pure MnCo₂O₄ as well (Figure 5 a, e and f). Both ORR and OER analysis reveals that
22 without the NGr support, pure MnCo₂O₄ exhibits poor electrocatalytic activity (Figure S6 in
23 Supporting Information). This is especially significant for ORR in which very negative onset
24 and half wave potentials of 0.7 and 0.6 V vs. RHE respectively, are observed. The reason
25 behind this is the poor electrical conductivity and weak oxygen binding/activating ability of
26 pure metal oxide.^[22] The order of activity in terms of half wave potential follows the pattern
27 observed in the CV plots i.e. MnCo₂O₄/NGr > Co_xO_y/ NGr > Mn₃O₄/NGr > NGr > pure

MnCo₂O₄. A summary of the electrocatalytic parameters of nanocatalysts is provided as Table S1 in supporting information.

ORR on the surface of electrocatalyst is possible by either an inefficient 2 or by more efficient 4 electron transfer pathway. To ascertain the pathway of ORR on the surface of MnCo₂O₄/NGr analysis was performed by recording the LSVs at different rotation rates and later plotting i/j against $1/\omega^{1/2}$ (Figure 5b and 5c). The selectivity of 4e⁻ or 2e⁻ pathway is estimated via Koutecky- Levich Equation.

$$1/j = 1/j_k + 1/j_L \quad (1)$$

Where j_k is the kinetic current density and j_L is the diffusion limiting current density.

Also

$$j_k = nFkC_o \quad (2)$$

And

$$j_L = 0.2nFC_oD_o^{2/3}v^{-1/6}\omega^{1/2} \quad (3)$$

Here ω is the angular velocity in rpm, n is transferred electron number, F is the Faraday constant 96485 C/mol, C_o is the bulk concentration of O₂ 1.15×10^{-3} mol/L, D_o is the diffusion coefficient of O₂ in electrolyte 1.9×10^{-5} cm²/s, v is the kinematic viscosity of the electrolyte 1.1×10^{-2} cm²/s and k is the electron-transfer rate constant. The linearity and parallelism of the koutecky–Levich slopes at different potentials (0.2-0.5 V vs. RHE) manifests 1st order reaction kinetics with respect to dissolved oxygen.^[23] The slope of the KL plots was further used to obtain the electron transfer number at different potentials. An electron transfer number of about 3.9 over a wide potential window manifest the dominance of 4 electron transfer pathway on the surface of MnCo₂O₄/NGr (inset Figure 5c). Comparative results for Co_xO_y/NGr, Mn₃O₄/NGr and NGr revealed electron transfer numbers of 3.61, 3.8 and 3.6 respectively. The mechanism of ORR catalytic activity on the MnCo₂O₄/NGr catalyst was further examined from the Tafel slope at low overpotential in O₂-saturated 0.1 M KOH

aqueous solution (Figure 5d). Generally for Pt/C, a Tafel plot i.e. V vs. $\log j_k$ shows two distinct slopes at low and high overpotentials, respectively.^[24] The two slopes can be described in term of the isotherms at two different oxygen coverages ; 1) at low overpotential the Temkin isotherm, which is associated with high O_2 coverage during ORR and a tafel slope value in the vicinity of 60 mV/dec, governs ORR, whereby the first electron transfer step involving an adsorbed product such as OH^- is the rate determining step ; and 2) at high overpotential the Langmuir isotherm marked with low O_2 coverage and a tafel slope of around 120 mV/dec directs ORR, wherein significant oxide coverage ceases to exist, which is generally the case when a two-electron transfer reaction is the rate-determining step. For Pt/C and $MnCo_2O_4/NGr$, tafel slopes of 85 mV/dec and 80 mV/dec respectively, manifests a temkin isotherm phenomenon to be dominant for ORR.

The ECSA of a catalyst plays a vital role in determining its activity towards ORR. For metal oxides loaded onto graphene, normalizing the double layer capacitance with the specific capacitance is a useful technique to get the ECSA according to Equation 4.^[25]

$$ECSA = C_{DL}/C_s \quad (4)$$

Non-Faradaic region was first identified and the $MnCo_2O_4/NGr$ loaded GCE was cycled at different scan rates in the potential window of 0.1 V in this region. The plot of scan rate vs. current has a linear relation for both anodic and cathodic scans according to Equation 5.

$$i_c = \nu C_{DL} \quad (5)$$

Where i_c is the capacitive current, ν is the scan rate and C_{DL} is the double layer capacitance. The slope of this plot was obtained and average of this slope was the double layer capacitance ' C_{DL} ' (Figure S7 in Supporting Information). ECSA was then estimated by normalizing double layer capacitance ' C_{DL} ' with the specific capacitance ' C_s '.^[25-26] Specific activity of the electrocatalysts at 0.85 V vs. RHE was then determined by dividing the kinetic current with the ECSA as tabulated in Table S1 and Figure S8 in Supporting Information. $MnCo_2O_4/NGr$

1 was found to have the largest value of SA compared to $\text{Co}_x\text{O}_y/\text{NGr}$, $\text{Mn}_3\text{O}_4/\text{NGr}$ and NGr . It
2 was about 1.5 times more than that of $\text{Co}_x\text{O}_y/\text{NGr}$, 8.5 times of $\text{Mn}_3\text{O}_4/\text{NGr}$ and 21 times
3
4 better than NGr . Moreover the mass activity also followed a similar trend i.e.
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6 $\text{MnCo}_2\text{O}_4/\text{NGr} > \text{Co}_x\text{O}_y/\text{NGr} > \text{Mn}_3\text{O}_4/\text{NGr} > \text{NGr}$. The superior catalytic activity of
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8 $\text{MnCo}_2\text{O}_4/\text{NGr}$ compared to the rest can be explained in terms of presence of mix valence of
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10 both manganese $\text{Mn}^{+2}/\text{Mn}^{+3}$ and cobalt $\text{Co}^{+2}/\text{Co}^{+3}$ in the cubic spinel MnCo_2O_4 .^[10] The
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12 introduction of transition metal cations in nitrogen doped carbons lead to the formation of
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14 $\text{M}-\text{N}-\text{C}$ bonds which provide these nano-materials high activity and stability in corrosive
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16 ORR environment.^[27] This finding is also in line with the recent report on Co-N-C moieties to
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18 be the active sites for ORR in metal coordinated with nitrogen enriched graphene shells.^[28]

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24 Apart from being highly active for ORR in alkaline media, $\text{MnCo}_2\text{O}_4/\text{NGr}$ was observed to be
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26 extremely active for oxygen evolution reaction as well (Figure 5e). $\text{MnCo}_2\text{O}_4/\text{NGr}$ was
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28 observed to have the most negative value of onset potential vs. RHE compared to Pt/C ,
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30 $\text{Co}_x\text{O}_y/\text{NGr}$, $\text{Mn}_3\text{O}_4/\text{NGr}$ and NGr . Moreover, $\text{MnCo}_2\text{O}_4/\text{NGr}$ had the smallest over potential
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32 to reach a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$. An important parameter to gauge the bifunctional
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34 ORR/OER activity of an electrocatalyst is the oxygen electrode activity ‘ ΔE ’ to reach a
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36 current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ for OER and $3 \text{ mA}\cdot\text{cm}^{-2}$ for ORR. This value was measured to
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38 be 0.91 V for the $\text{MnCo}_2\text{O}_4/\text{NGr}$ which is better than a number of similar metal oxides
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40 deposited onto graphene.^[21a, 21b, 29] The value of ΔE for $\text{Co}_x\text{O}_y/\text{NGr}$, NGr and Pt/C was found
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42 to be 1.04 , 1.31 and 1.07 V respectively (Figure 5f). Mn_3O_4 decorated graphene was observed
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44 to be a poor OER catalyst as it was unable to achieve a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$.
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51 Apart from high activity and low cost another desirable feature of ORR electrocatalyst is long
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53 term durability in the corrosive alkaline media. For example, Pt/C on carbon is highly active
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55 for ORR but it is also highly instable in alkaline media.^[6] Over course of time particle
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57 agglomeration, coarsening and leaching into the electrolytes have been identified as possible
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59 degradation causes for Pt/C . To address this issue, both short term stability (amperometric i-t
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1 test) and long term durability (accelerated durability test ADT) tests were conducted on
2 MnCo₂O₄/NGr. The superior stability of MnCo₂O₄/NGr and huge instability of Pt/C is clearly
3 evident from the i-t test performed at constant potential of 0.665 V vs. RHE for both catalysts
4 under O₂ saturated alkaline environment (**Figure 6a**). A 22% decrease in the initial value of
5 current was observed for Pt/C over a short period of time which is in agreement with other
6 reports on Pt/C.^[21b, 30] On the other hand for MnCo₂O₄/NGr a very small loss of 3% in
7 normalized current was noted under the same conditions. This trend was also present in the
8 LSV data recorded before and after the amperometric i-t test (Figure 6b). The reason behind
9 the high stability of the MnCo₂O₄/NGr compared to commercial Pt/C can be understood by
10 the presence of coordination of the spinel oxide and N doped sites of the nitrogenized
11 graphene. The incorporation of nitrogen in the graphene host has been reported to provide
12 anchoring sites for the metal oxide NPs forming M—N—C bonds which resist the particle
13 dissolution or growth during the ORR.^[10, 29] The long term durability of MnCo₂O₄/NGr in
14 alkaline media was further assessed by subjecting it to 1000 potential sweeps from 0.6 to 1 V
15 vs. RHE. The LSVs were recorded in a periodic manner as shown in (Figure 6c). A loss of
16 only 17 mV in half-wave potential after 1000 cycles manifests the excellent durability of the
17 MnCo₂O₄/NGr in alkaline media supporting its candidacy as an efficient, active and stable
18 electrocatalyst for ORR in metal-air battery and alkaline fuel cells (Figure 6d).

19 To translate the superior activity and stability MnCo₂O₄/NGr in alkaline condition into an
20 energy conversion device, we employed it as an ORR catalyst in a home built primary Zn-air
21 battery. For comparison commercial Pt/C was also coated on a carbon paper and used in a Zn-
22 air battery. The discharge polarization curves along with power density data for both are
23 provided in **Figure 7a**. It is noteworthy to mention that both the plots were recorded from the
24 battery working in ambient air environment which is a more realistic approach to simulate the
25 real life scenario. Moreover testing the Zn-air battery under ambient static air condition is
26 much more practical than testing it with blowing oxygen or water vapor saturated ideal

1 conditions because of the fact that both the intrinsic activity and architecture of catalysts are
2 sensitive to oxygen and electrolyte diffusion which contributes to the overall cell
3 performance.^[31] The primary Zn-air batteries had an open circuit voltage (OCV) of 1.55 V
4 and 1.50 V respectively for commercial Pt/C and MnCo₂O₄/NGr respectively. The behavior
5 of the discharge profiles reveal an activation loss region followed by an ohmic loss region.
6
7 The activation loss section is associated with potential loss due to the activation barrier that a
8 reactant species must overcome whereas the ohmic loss part shows the loss due to the
9 electrical resistance of the components. Pt/C cathode based battery was observed to have a
10 maximum power density of 94.6 mW.cm⁻² at a current density of 100 mA.cm⁻² along with a
11 current density of 85 mA.cm⁻² at a discharge voltage of 1.0 V. These values are in agreement
12 with the data reported for primary Zn-air battery working in ambient air by other
13 researchers.^[32] MnCo₂O₄/NGr was observed to have a maximum power density of 87
14 mW.cm⁻² at a current density of 100 mA.cm⁻² along with a current density of 70 mA.cm⁻² at a
15 discharge voltage of 1.0 V. The close resemblance in polarization plots for primary Zn-air
16 batteries made from Pt/C and MnCo₂O₄/NGr are in agreement with their LSV data described
17 earlier. In order to assess the long term galvanostatic discharge behavior of MnCo₂O₄/NGr
18 loaded Zn-air battery, we operated the battery at medium to high discharge current densities
19 i.e 20-40 mA.cm⁻² (Figure 7b). The battery was observed to function with stable voltages of
20 1.2, 1.15 and 1.1 V for discharge loads of 20, 30 and 40 mA.cm⁻² respectively, for a prolong
21 period of time. These values are superior than the Zn-air battery made from graphene
22 supported CoMn₂O₄ (CMO) nanoparticles, Mn, Co co-substituted Fe₃O₄ nanoparticles on
23 nitrogen doped reduced graphene and NiCo alloy with their mixed oxides on carbon
24 nanotubes (CNT).^[29, 33] The slight decrease in cell voltage with current density can be
25 explained by the formation of insulating ZnO with high discharge current as explained
26 elsewhere in literature.^[9, 34] The final drop in the voltage was due to the consumption of Zn
27 metal anode over the period of time. MnCo₂O₄/NGr loaded Zn-air battery was also observed

1 to have a high specific capacity with a stable voltage profile (Figure 7c). The capacity for the
2 battery was obtained by normalizing the energy retrieved from the battery ‘Ah’ with the mass
3 of zinc consumed at different current densities. For the MnCo₂O₄/NGr loaded battery a
4 specific capacity of 707 mAh.g⁻¹_{Zn} was observed at a discharge current density of 40 mA.cm⁻².
5
6 The capacity of the MnCo₂O₄/NGr derived Zn-air battery was better compared to the
7 discharge capacities reported in several similar Zn-air systems and even comparable to the
8 more recently introduced hybrid Ni-Zn hybrid air system.^[9, 16, 33a] Most strikingly the
9 MnCo₂O₄/NGr loaded Zn-air battery was found to be functioning with the same capacity by
10 only replenishing the consumed Zn anode and electrolyte after each discharge (Figure 7d). By
11 refueling the battery periodically, MnCo₂O₄/NGr derived Zn-air battery was observed to
12 function with a stable discharge profile for a time period of more than 24 hrs. This result is in
13 agreement with its high stability and durability data found for the MnCo₂O₄/NGr in alkaline
14 environment.

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16 The exceptional ORR and OER activity of MnCo₂O₄/NGr was further translated into a
17 rechargeable zinc air battery. The MnCo₂O₄/NGr loaded zinc air battery was observed to
18 function with extremely stable charge-discharge profile compared to commercial Pt/C
19 (**Figure 8 a, b**). For MnCo₂O₄/NGr, small charge discharge potential gap (CD) of 0.64 V at j
20 of 1 mA.cm⁻² for the 1st cycle compared to 0.72 V for Pt/C demonstrates its superior
21 bifunctional activity. Furthermore CD value for Pt/C was observed to increase with
22 time/cycles demonstrating the poor cyclic performance of Pt/C for rechargeable Zn-air battery.
23 At the end of 100th cycle CD was measured to be 0.87 V for Pt/C. A similar decline in
24 performance for Pt/C have been reported which can be understood by the careful examination
25 of stability/durability data.^[12, 33a] Possible causes have been identified as oxidation of support,
26 particle agglomeration and dissolution in highly alkaline electrolyte.^[6] This leads to higher
27 charge voltage and lower discharge voltage with continuous operation accompanied with the
28 increase of CD gap (Figure 8 a, b). Contrary to this, MnCo₂O₄/NGr was observed to function

1 with extremely stable charge-discharge profile. The CD gap of 0.63 V after 100 cycles
2 validates the superior activity and stability of MnCo₂O₄/NGr for rechargeable zinc air system.
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4 Furthermore the round-trip efficiency changed by only 0.3% after 100 cycles from initial
5 value of 65.8% to final value of 66.1%. The superior performance of MnCo₂O₄/NGr
6 rechargeable Zn-air battery is justified by its electrochemical and durability test data which
7 confirms the stable and good ORR/OER performance in alkaline media compared to
8 commercial Pt/C.
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11 A close examination of the charge-discharge behavior reveals a distinct phenomenon
12 compared to conventional step-cyclic behavior as in Pt/C. Unlike a single plateau
13 charge/discharge profile for OER/ORR, humps in charge-discharge cycle was observed
14 indicating presence of supercapacitive behaviour in MnCo₂O₄/NGr rechargeable Zn-air
15 battery (Figure 8c). The charging cycle reveals a distinct hump at 1.75 V over MnCo₂O₄/NGr
16 surface followed by the plateau for OER. A similar hump during discharge cycle was also
17 found for MnCo₂O₄/NGr. This is in contrast to commercial Pt/C for which a single plateau for
18 OER was observed over the charging cycle (Figure 8d). The deviation of the charge-discharge
19 behavior in MnCo₂O₄/NGr compared to commercial Pt/C can be understood by the
20 occurrence of metal oxide oxidation-reduction along with ORR/OER. A similar charge-
21 discharge phenomenon is also reported for nickel cobalt oxide supported on carbon coated
22 nickel foam NiCo₂O₄/NiF@C.^[15] This transition of metal oxide to hydroxide during charging
23 and conversion to oxide from hydroxide during discharge was observed to improve the
24 charge-discharge cyclic efficiency ‘ η ’ measured as the ratio of energy delivered on discharge
25 to energy consumed on charge. For the 5th cycle, MnCo₂O₄/NGr Zn-air battery consumed 0.43
26 Wh for charging and delivered 0.36 Wh on discharge with η of 83.7% (Figure S9 in
27 Supporting Information). Compared to this, Pt/C consumed more Wh during charging and
28 delivered less on discharge for the same cycle thus resulting in a lower cyclic efficiency of
29 63.9%. More interestingly with the passage of time/cycles, η was observed to deteriorate for
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1 Pt/C. η values of 61.2 and 58.9 measured for 20th and 40th charge-discharge cycle respectively
2 confirms the instability of Pt/C for rechargeable zinc-air battery. η values of 86 and 86.5 %
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4 for the 20th and 40th charge-discharge cycles in case of MnCo₂O₄/NGr derived zinc battery
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6 confirms its superior bifunctional activity and stability. The redox transitions M-O \leftrightarrow M-O-OH
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8 can induce hybrid behavior in in MnCo₂O₄/NGr derived zinc-air battery. These transitions
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10 cause lower energy consumption i.e Wh on charge and renders more Wh during the discharge
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12 cycle compared to conventional Zn-air battery (Figure 8e). Apart from better cyclic efficiency,
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14 MnCo₂O₄/NGr hybrid battery operates at a higher voltage and delivers larger power density
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16 during each cycle (Figure 8f). Moreover this charge-discharge behavior is also evident at
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18 higher current densities of 5 and 10 mA.cm⁻² (Figure S10 in Supporting Information).
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20 MnCo₂O₄/NGr hybrid battery was observed to function with a stable profile for over 150
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22 cycles with a low charge discharge gap of 0.81 V and cyclic efficiency of 75%. More
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24 importantly the cyclic efficiency was also stable over the 150 cycles for hybrid MnCo₂O₄/NGr
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26 battery. The charge discharge gap for MnCo₂O₄/NGr hybrid battery is lower by 0.2 V at the
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28 same current density compared to recently reported NiCo₂O₄/NiF@C hybrid battery. Pt/C on
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30 the other hand was observed to be highly instable as observed by increasing charge discharge
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32 gap with cycles. Again at higher current density, MnCo₂O₄/NGr battery was able to deliver
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34 higher power density during discharging as shown in Figure S10d in Supporting Information.
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36 This can be associated with the supercapacitive properties of MnCo₂O₄/NGr which allow it to
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38 work at higher voltage and as such provide high power density and high energy density.
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42 In order to investigate the reason behind the excellent cyclic efficiency and high power
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44 density of MnCo₂O₄/NGr, we also analyzed its supercapacitive behavior and found that in
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46 addition to having remarkable ORR/OER activity and stability, MnCo₂O₄/NGr was observed
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48 to display remarkable super capacitive properties as well. **Figure 9a** shows the current
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50 response of MnCo₂O₄/NGr coated Ni-foam against different scan speeds. The strong response
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52 with scan rates shows the excellent capacitive nature of the MnCo₂O₄/NGr. For reference, the
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CV of Ni-Foam current collector was also added which shows its negligible response with scan speeds. The specific capacitance at different scan speeds (Figure 9b) was then calculated by Equation (6).

$$C = \int I \cdot dt / m \cdot \Delta V \quad (6)$$

Where I is the reduction/oxidation current, dt is time differential, m is the mass of active material and ΔV is the voltage range of reduction/oxidation sweep segment. MnCo₂O₄/NGr nanocomposite was observed to display a high specific capacitance of 585 F.g⁻¹ at a scan speed of 5 mV.s⁻¹ based on the total sample mass. Even at a very high scan rate of 50 mV.s⁻¹, specific capacitance of 314 F.g⁻¹ was recorded for MnCo₂O₄/NGr. These values are comparable/superior to a number of similar metal oxides on graphene composites reported by different processing routes.^[35] Apart from CV, charge-discharge analysis at different current densities also confirmed the excellent super capacitive nature of MnCo₂O₄/NGr (Figure 9c). MnCo₂O₄/NGr showed high specific capacitance of 591.2 F.g⁻¹ at charge-discharge current density of 1 A.g⁻¹. In order to confirm the durability, MnCo₂O₄/NGr loaded Ni-Foam was cycled for 1000 times at a high charge-discharge current density of 5 A.g⁻¹ (Figure 9d). Figure S11a in Supporting Information displays the CV curves before and after 1000 cycles at 5 A.g⁻¹. From Equation 6, the specific capacitance was estimated to be 295 F.g⁻¹ at 50 mV/s which shows a small decrease i.e. 6% compared to the initial value of 314 F.g⁻¹. Ragone Plot (power density vs. energy density) demonstrates the excellent energy storage capability of MnCo₂O₄/NGr (Figure S11b in Supporting Information). A high power density of 5 kW/kg⁻¹ along with good energy density of almost 20 Wh.kg⁻¹ confirms the suitability of the MnCo₂O₄/NGr to be used for energy storage and conversion applications. The supercapacitive nature of MnCo₂O₄/NGr along with its inherent ORR/OER catalytic ability allows the hybrid battery to operate at higher working voltage, high power density and excellent cyclic efficiency compared to conventional Zn-air battery.

3. Conclusion

To conclude, we report a simple and facile hydrothermal route for the synthesis of non-noble metal oxide nanoparticles on graphene. The uniform dispersion of cubic spinel MnCo_2O_4 was confirmed by SEM and TEM. The combined mix valence of $\text{Mn}^{+2/+3}$ and $\text{Co}^{+2/+3}$ in MnCo_2O_4 provides higher catalytic activity to MnCo_2O_4 for ORR compared to individual cobalt or manganese oxides. Apart from high activity, $\text{MnCo}_2\text{O}_4/\text{NGr}$ was observed to be highly stable and durable in alkaline environment. We demonstrated the application of $\text{MnCo}_2\text{O}_4/\text{NGr}$ as a cathode catalyst for a primary Zn-air battery working under realistic ambient conditions. The discharge profile of $\text{MnCo}_2\text{O}_4/\text{NGr}$ derived Zn-air system was observed to be comparable to the commercial Pt/C along with a high discharge capacity of $787 \text{ mAh.g}^{-1}_{\text{Zn}}$ at a current density of 20 mA.cm^{-2} . The $\text{MnCo}_2\text{O}_4/\text{NGr}$ catalyzed mechanical rechargeable Zn-air battery was observed to be refueled and function regularly with no loss in performance which is in agreement with its stability data. Additionally, the $\text{MnCo}_2\text{O}_4/\text{NGr}$ was observed to display exceptional super capacitive properties with a good discharge capacity of 591.2 F.g^{-1} at discharge current density of 1 A.g^{-1} . By synergizing the electrocatalytic and supercapacitive behavior of $\text{MnCo}_2\text{O}_4/\text{NGr}$, we report a highly stable, efficient and high power hybrid zinc-air battery with low charge-discharge potential gap and exceptional cyclic efficiency of 86% over 100 charge-discharge cycles at 1 mA.cm^{-2} . In brief, by synergizing the electrocatalytic and supercapacitive nature of electrocatalyst, we demonstrate that highly active, stable and efficient advanced zinc air batteries can be developed.

4. Experimental Section

Chemicals: cobalt (II) acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_4 \cdot 4\text{H}_2\text{O}$, > 99.5%) and potassium hydroxide (KOH) procured from Guangdong chemicals, Manganese acetate tetrahydrate ($\text{Mn}(\text{CH}_3\text{COO})_4 \cdot 4\text{H}_2\text{O}$, > 99%), Ammonia solution (25-27%) and Zinc strips (Zn, 99.99%) from Tianjin Fuchen, Platinum on carbon (Pt/C, 20%) from Johnson Matthey fuel cells,

1 Nafion ionomer solution (5%) from Dupont and carbon fiber paper (HCP 120) from Hesen
2 Shanghai Electric, Graphene oxide (GO) solution with concentration 5mg/mL from Tanfeng
3 technology Inc. and Ethanol (C₂H₅OH, >99.7%) from Tianjin Fuyu chemicals. All the
4 Electrolyte solutions were prepared with ultra-pure distilled water (18.25 MΩ.cm⁻¹).
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9 *Calculation synthesis:* Manganese cobalt oxide (MnCo₂O₄) nanoparticles supported on nitrogen
10 doped reduced graphene oxide i.e. MnCo₂O₄/NGr was synthesized by hydrothermal method.
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12 In brief, 0.222 mM of cobalt acetate and 0.111 mM of manganese acetate were mixed with 27
13 mL DI for MnCo₂O₄/NGr, followed by stirring for 15 minutes at room temperature. To this 13
14 mL of GO (5mg/mL) was added and the stirring was continued for 2 hrs. At this point, 0.5 mL
15 of 27% NH₃ solution was added to above and the temperature of the bath was raised to 80 °C.
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17 Stirring was continued for another 24 hrs followed by which the precursor solution was
18 transferred to a Teflon lined SS autoclave. The autoclave was placed at 150 °C for 3 hrs in an
19 oven for hydrothermal treatment. After the heat cycle, autoclaves were allowed to cool
20 naturally in the oven. The solid product was then washed several times with DI and collected
21 by centrifugation. Finally, MnCo₂O₄ on graphene were collected by freeze drying and
22 designated as MnCo₂O₄/NGr. Co_xO_y/NGr and Mn₃O₄/NGr were also made by the same
23 process by simply using only 0.333 mM of each corresponding salt. NGr was made by
24 treating GO with 0.5 mL of 27% NH₃ solution in the same way without using any metallic
25 salt.
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45 *Crystal structure characterization:* The crystal structure of the catalysts was
46 characterized by using X-ray diffraction (XRD) with Cu Ka radiation on PANalytical X'Pert
47 Pro MPD. The working potential and current employed were 40 KV and 40 mA, respectively.
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49 The morphological and structural features of nanocatalysts were observed via field emission
50 scanning electron microscopy (SEM, FEI NovaSEM 450) and high-resolution transmission
51 electron microscopy (HRTEM, FEI Tecnai F30) at 200 kV. DSC/TGA analysis was done in
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an oxygen environment by heating at a temperature ramp of 10 °C/min from room temperature to 800 °C on NETZSCH STA 449 F3 thermal analyzer.

Electrochemical characterization: All electrochemical measurements were carried out on a classic three electrode set-up. The Hg/HgO (1 M KOH, 0.098V vs. SHE) was used as a reference electrode, Pt wire was used as a counter electrode and the working electrode was fabricated by depositing catalyst inks onto a rotating glass carbon electrode (GCE) with a diameter of 5mm. CHI660C electrochemical workstation was used to measure the catalytic activity of catalysts. Cyclic voltammetry (CV) was done in both N₂ and O₂ saturated 0.1 M KOH. Prior to recording of data, N₂ or O₂ was bubbled through the electrolyte for at least 15 minutes. Catalyst ink for CVs and LSVs was made by adding 4 mgs of catalyst to a mixture of ½ mL of ethanol, ½ mL of DI and 10 µL of 5% Nafion ionomer solution. The ink was subjected to sonication for 30 mins and later 5µL of this ink was drop cast onto GCE and air dried for 10 minutes followed by heating in oven for 5 minutes at 50 °C. The catalyst loading on GCE was estimated to be 0.1 mg.cm⁻². Linear Scan Voltammetry (LSV) was performed on the thin film of catalyst nanoparticles deposited on GCE at room temperature in 0.1 M KOH (O₂ saturated). The experiments were performed at a scanning rate of 10 mV.s⁻¹ with the rotation rates of 900, 1600, 2500 and 3200 rpm. The measured current was normalized to the geometric area of the catalyst layer on GCE and the potentials were converted to reversible hydrogen electrode (RHE) scale according to Nernst equation; $E_{RHE} = E_{Hg/HgO} + 0.098 + 0.059 \cdot pH$.

Zn-air batteries: Zn-air batteries were made according to a home designed cell configuration. For primary and mechanically rechargeable Zn-air battery; catalyst ink was made by adding 4 mgs of catalyst powder with 2 mgs of Vulcan XC-72 followed by dispersion in a solution of 1 mL ethanol and 40 µL 5% nafion ionomer. After sonication for 30 mins, this ink was drop casted onto hydrophobic carbon paper to get a catalyst loading of 1.2 mg.cm⁻². The carbon paper was later dried for 30 mins at 70 °C and later coupled with a zinc foil through 6 M KOH

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to form a Zn-air cell. Porous glass membrane was used as a separator between anode and air-cathode. For rechargeable $\text{MnCo}_2\text{O}_4/\text{NGr}$ derived zinc air battery, nickel foam was first cleaned with dilute sulfuric acid for 15 min and soaked in acetone solution for 2 hours. The nickel foam current collector was then washed with deionized water and dried in oven at 70 °C for 2 hrs. The cleaned nickel foam was finally placed into the Teflon lined autoclave for direct hydrothermal deposition of $\text{MnCo}_2\text{O}_4/\text{NGr}$. After hydrothermal treatment, nickel foam was washed several times with DI to remove loose particles. Subsequently $\text{MnCo}_2\text{O}_4/\text{NGr}$ deposited nickel foam was dried at 70 °C for 2 hrs. Gas diffusion layer (GDL) was made by mixing 0.5 g of acetylene black, 2.5 ml of PTFE (65%) and 15 ml of absolute ethanol with 5 ml of deionized water and stirring was done for 3 hours to form a colloidal solution. This colloidal solution was separated in an ultrasonic bath for 15 minutes and bath was heated at 80 °C water for 10 minutes to get the acetylene black colloid. The gas diffusion layer (0.5 mm thick) was obtained by drying this colloid and pressing at 10 MPa pressure for 30 min. To prepare the air electrode, $\text{MnCo}_2\text{O}_4/\text{NGr}$ loaded nickel foam and GDL were rolled to a thickness of 0.5 mm and dried for 30 min at 70 °C. The air electrode was coupled to zinc strip anode via 6 M KOH + 0.2 M zinc acetate electrolyte in a home built cell. The performance of the zinc-air batteries was measured and recorded through a battery testing system CT 2001A (LANHE Company) in ambient atmosphere. Battery testing and cycling experiments were performed at 25 °C and 1 atmosphere.

The working electrode for supercapacitor test was prepared by mixing MnCo₂O₄/NGr, Acetylene black and Polytetrafluoroethylene (60 wt%) with a mass ratio of 80:10:10. MnCo₂O₄/NGr and Acetylene black were first ground and added to DI to form slurry to which PTFE was subsequently added. The ink was then coated onto nickel foam which was used as a current collector and pressed at 10 MPa followed by drying overnight at 70 °C. All electrochemical experiments were carried out in 6 mol·L⁻¹ KOH using a three-electrode system, in which platinum wire and Hg/HgO electrodes were used as counter and reference electrodes, respectively. Cyclic voltammetry (CV) tests and galvanostatic charge-discharge measurements were performed on a CHI660C electrochemical workstation. Cyclic stability was performed by 1000 charge-discharge cycles at 5 A.g⁻¹, after which the 6M KOH was replaced with fresh solution and then CV was recorded at 50 mV.s⁻¹.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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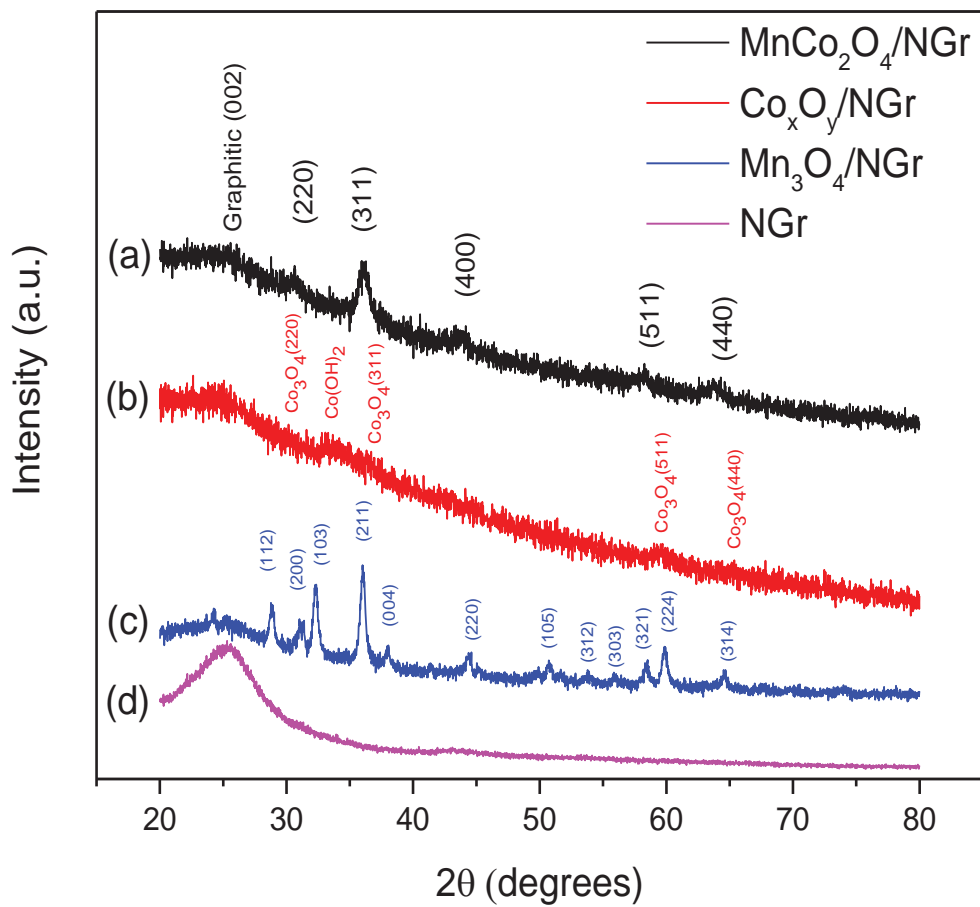


Figure 1 XRD patterns of (a) MnCo₂O₄/NGr, (b) Co_xO_y/NGr, (c) Mn₃O₄/NGr and (d) NGr.

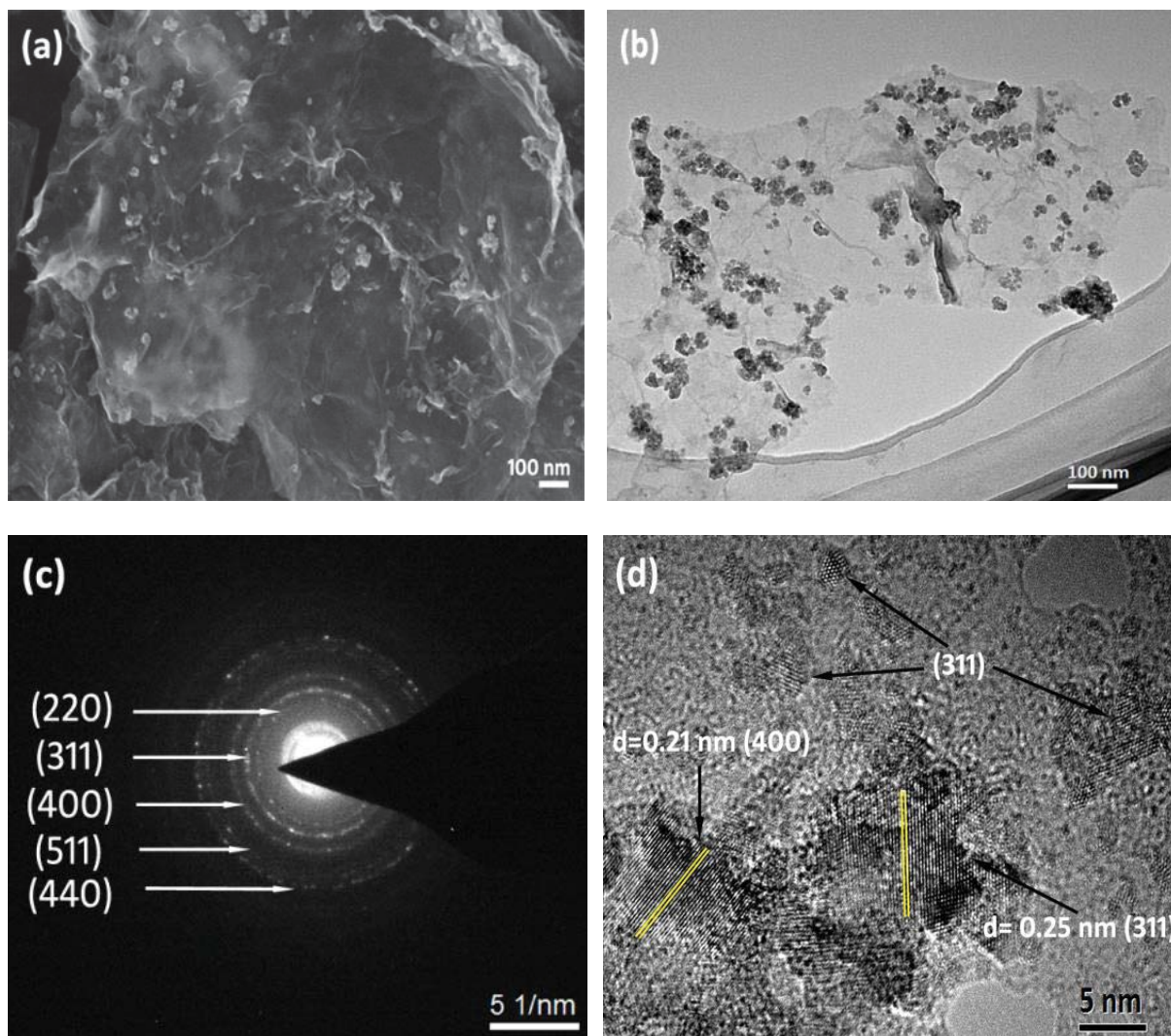


Figure 2 Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis of MnCo₂O₄/NGr. (a) Low-magnification SEM image. (b) Low-magnification TEM image. (c) Selected Area Electron diffraction SAED. (d) High-resolution TEM.

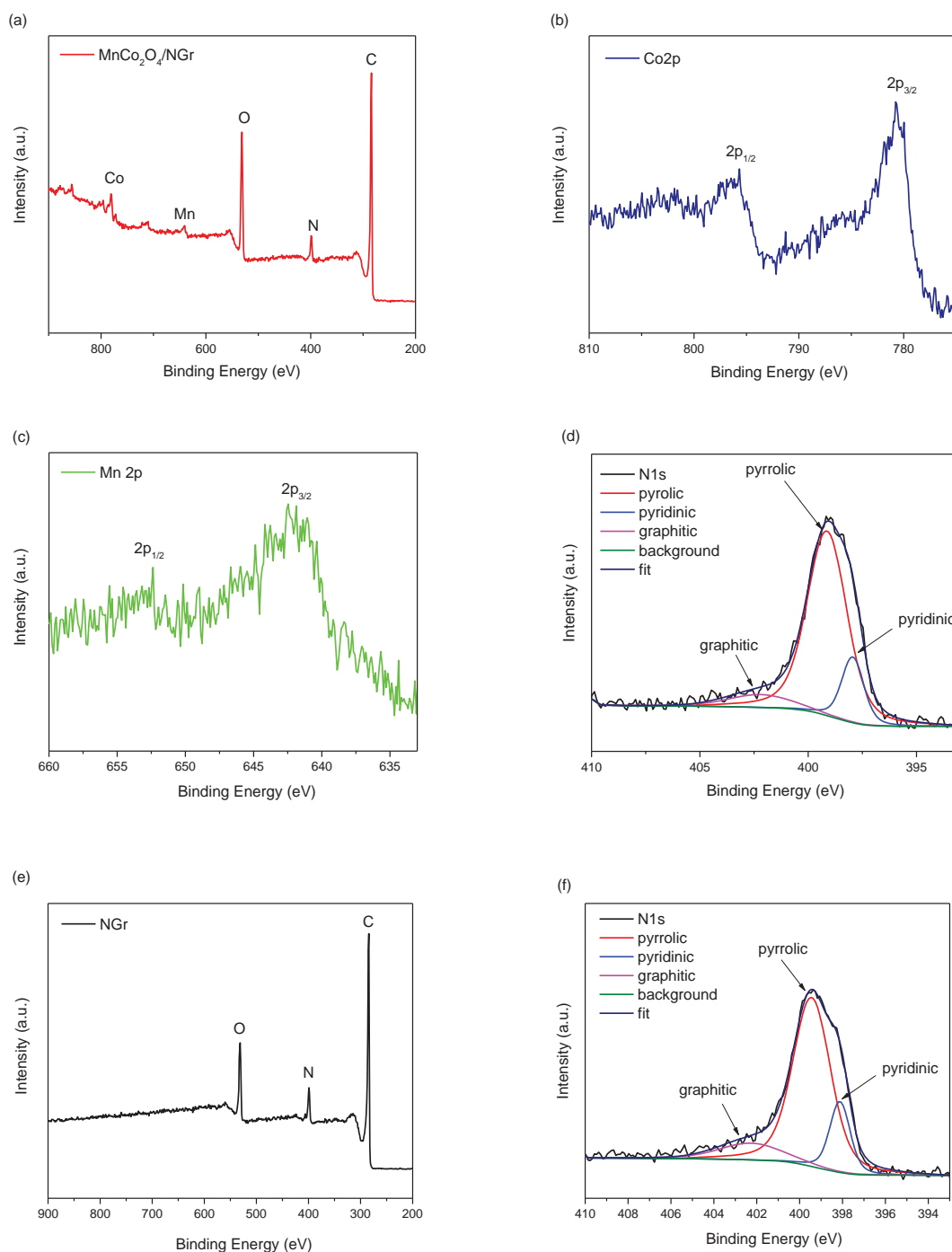


Figure 3 XPS analysis of MnCo₂O₄/NGr (a-d) and NGr (e,f). (a) Survey spectra of MnCo₂O₄/NGr. (b) High resolution Co2p of MnCo₂O₄/NGr. (c) High resolution Mn2p of MnCo₂O₄/NGr. (d) High resolution N1s of MnCo₂O₄/NGr with peak deconvolution to reveal different N contents. (e) Survey spectra of NGr. (f) High resolution N1s of NGr with peak deconvolution.

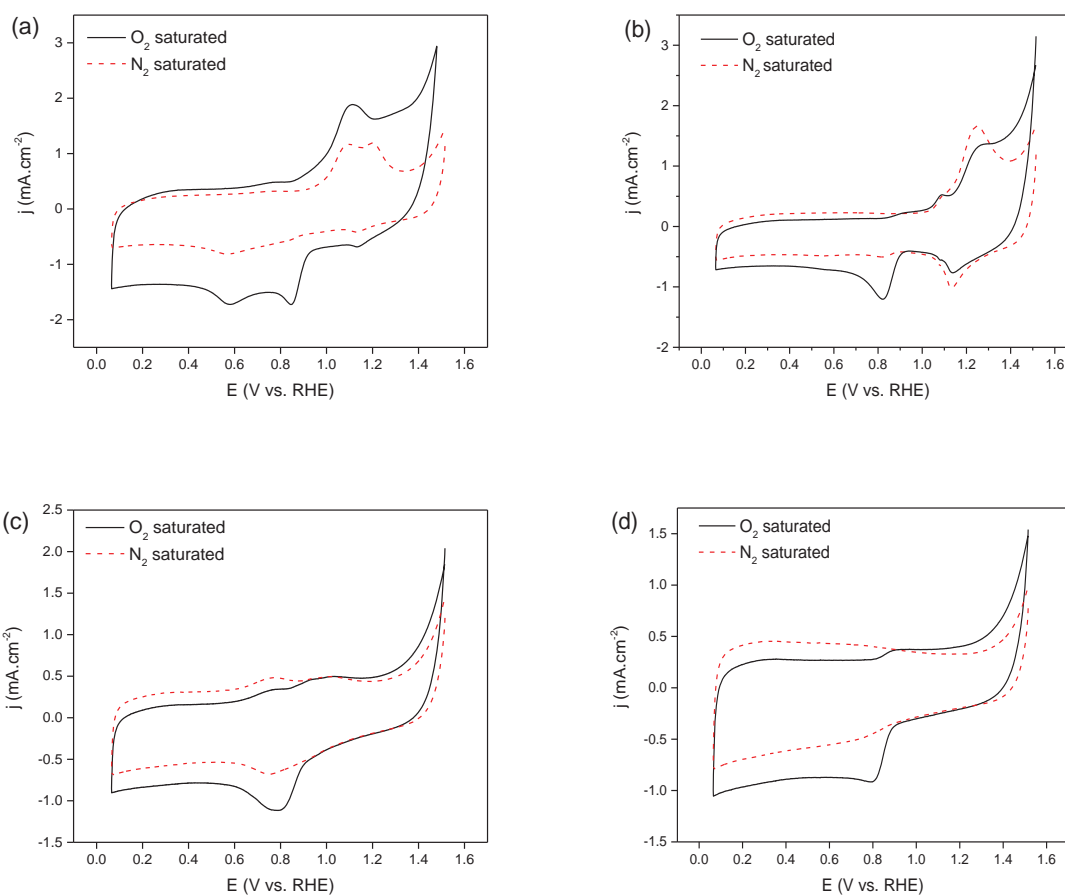


Figure 4 Cyclic voltammetry (CV) of electrocatalysts in O_2 saturated (black solid line) and N_2 saturated (red dashed line) in 0.1 M KOH. (a) $\text{MnCo}_2\text{O}_4/\text{NGr}$, (b) $\text{Co}_x\text{O}_y/\text{NGr}$, (c) $\text{Mn}_3\text{O}_4/\text{NGr}$ and (d) NGr .

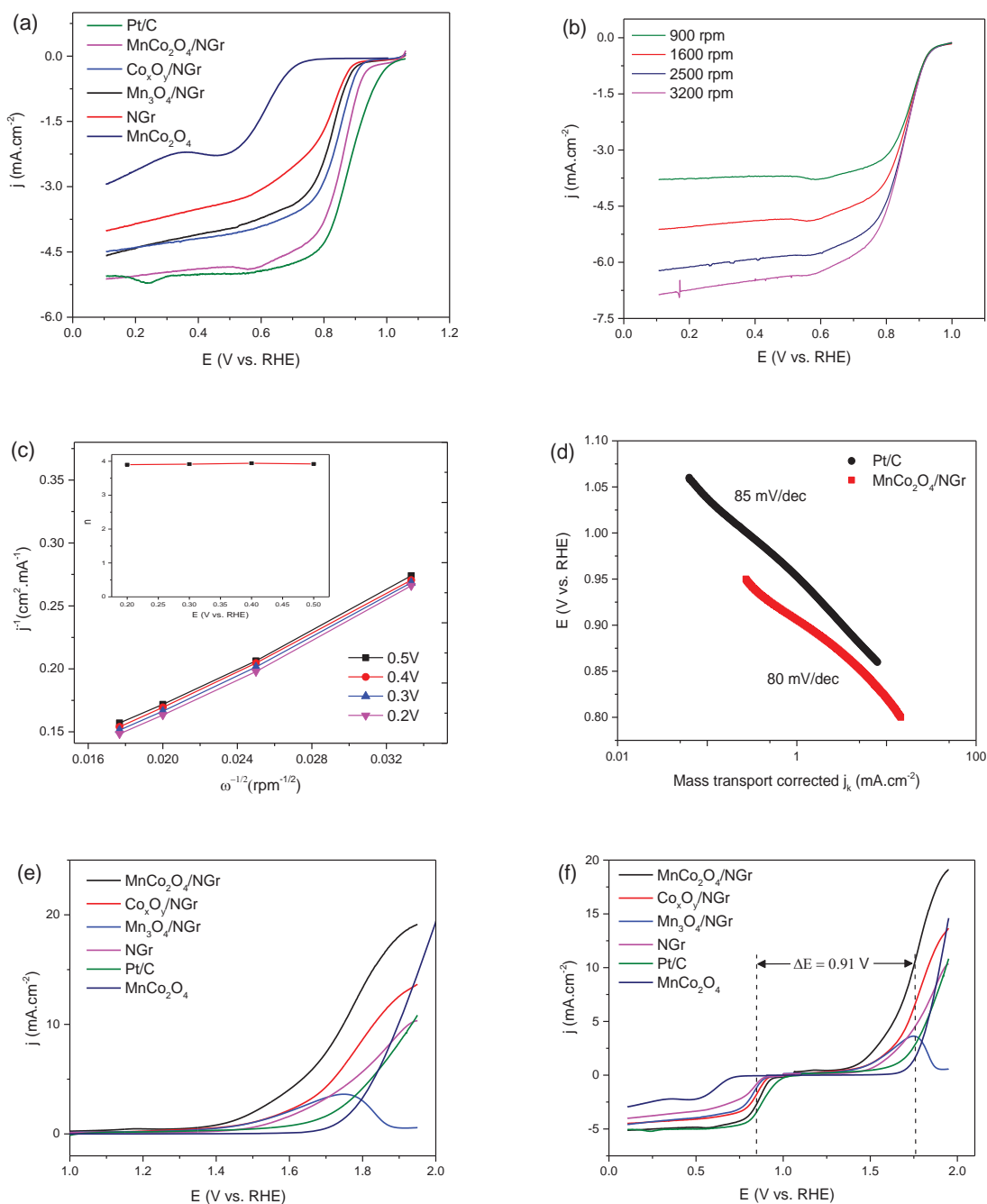


Figure 5 Linear scan voltammetry (LSV) data. (a) LSV of electrocatalysts at 1600 rpm in O₂ saturated 0.1 M KOH, (b) LSV of MnCo₂O₄/NGr at 900, 1600, 2500 and 3200 rpm in O₂ saturated 0.1 M KOH, (c) Koutecky-Levich plots of MnCo₂O₄/NGr with electron transfer number at different potentials (inset) and (d) Mass transport corrected Tafel plots for MnCo₂O₄/NGr and Pt/C. (e) LSV for OER of electrocatalysts at 1600 rpm in O₂ saturated 0.1 M KOH. (f) ORR and OER together to calculate ΔE for electrocatalysts.

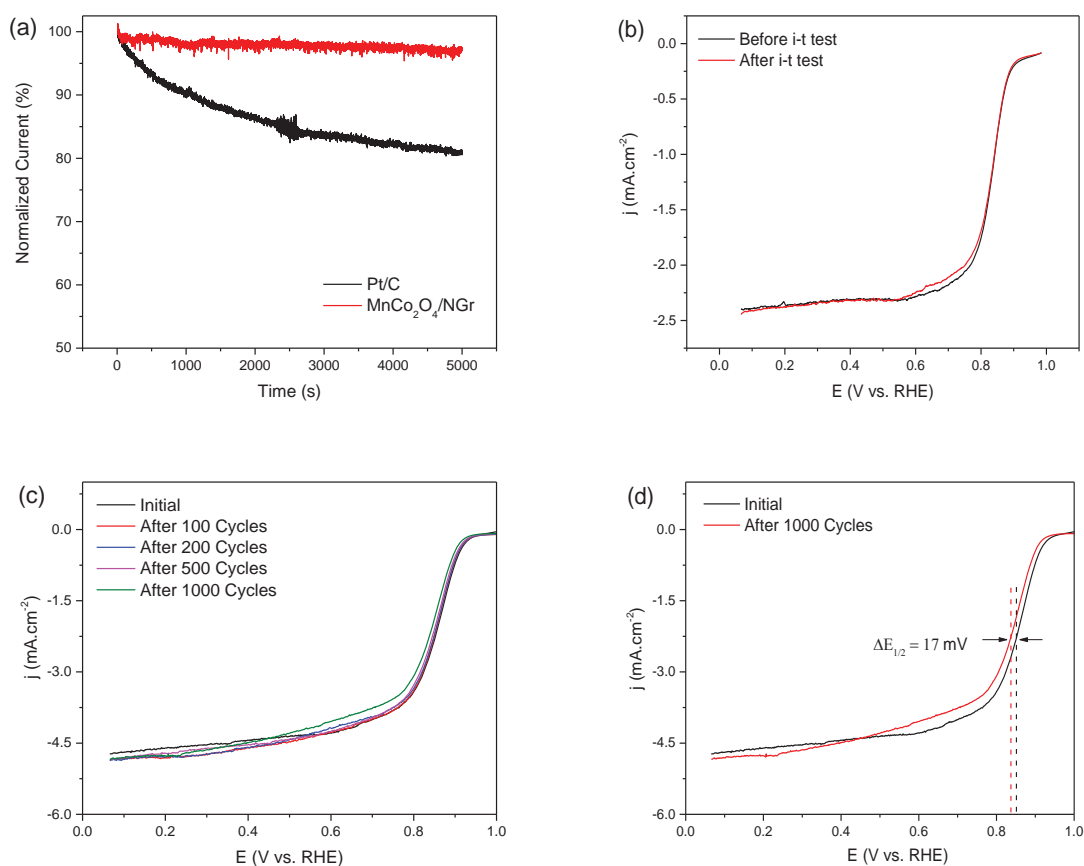


Figure 6 Stability and durability performance. (a) Amperometric i-t plots for MnCo₂O₄/NGr and commercial Pt/C in O₂ saturated 0.1 M KOH at 400 rpm and 0.665 V vs. RHE, (b) LSV comparison before and after i-t test for MnCo₂O₄/NGr in O₂ saturated 0.1 M KOH at 400 rpm, (c) Accelerated durability test (ADT) on MnCo₂O₄/NGr ; initial LSV and after 100, 200, 500 and 1000 potential cycles. (d) LSV comparison before and after ADT on MnCo₂O₄/NGr at 1600 rpm in O₂ saturated 0.1 M KOH.

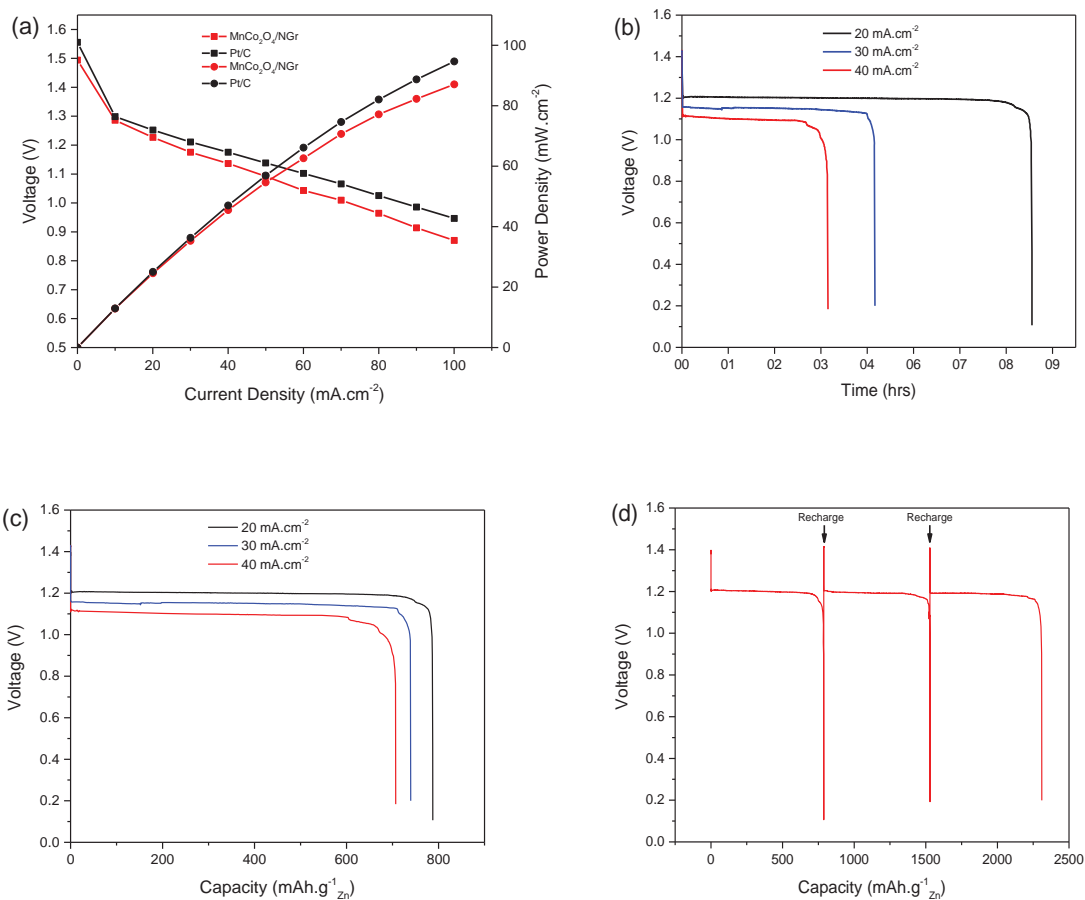


Figure 7 Zinc-air battery performance. (a) Cell voltage and power density polarization curves of a primary zinc-air battery working in ambient air. (b) Discharge profile at current densities of 20, 30 and 40 mA.cm⁻², respectively. (c) Specific capacity of the zinc-air battery at 20, 30 and 40 mA.cm⁻², respectively and (d) Mechanical rechargeable Zinc-air battery performance at 20 mA.cm⁻². The cathode is same MnCo₂O₄/NGr while Zn anode and 6M KOH electrolyte are replaced regularly as indicated by the arrows

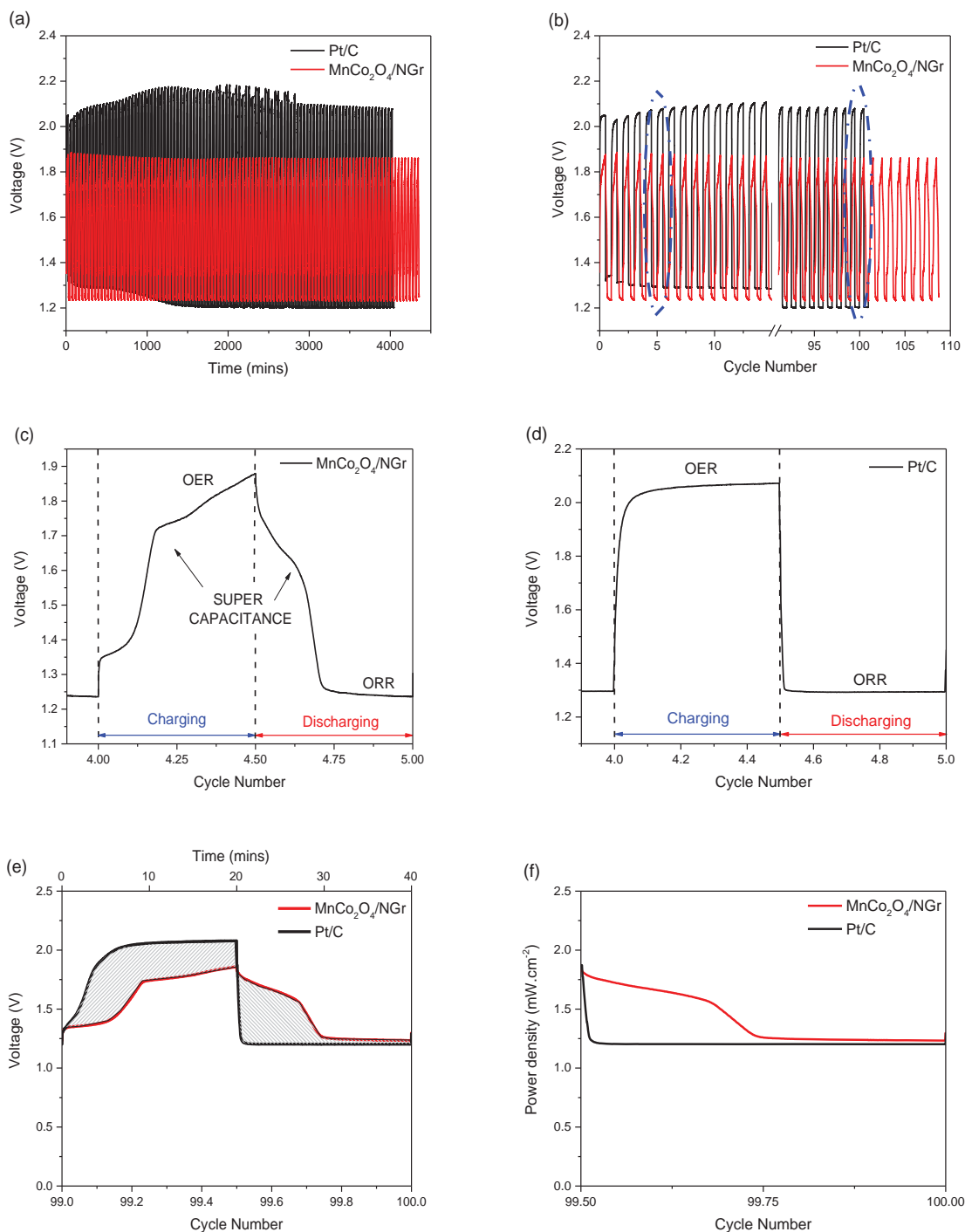


Figure 8 Rechargeable zinc air battery. (a) charge-discharge behavior with time for MnCo₂O₄/NGr (red) and Pt/C (black) at 1mA.cm⁻² with 20 mins charge and 20 mins discharge. (b) overall charge-discharge profile of Zn-air battery for >100 cycles. (c) charge-discharge behavior of MnCo₂O₄/NGr at 5th cycle. (d) charge-discharge behavior of Pt/C at 5th cycle. (e) charge-discharge behavior of MnCo₂O₄/NGr (red) and Pt/C (black) at 1mA.cm⁻² for 100th cycle; shaded region shows the less Wh intake during charge and more Wh delivered during discharge by MnCo₂O₄/NGr hybrid battery. (f) power density delivered during 100th discharge cycle.

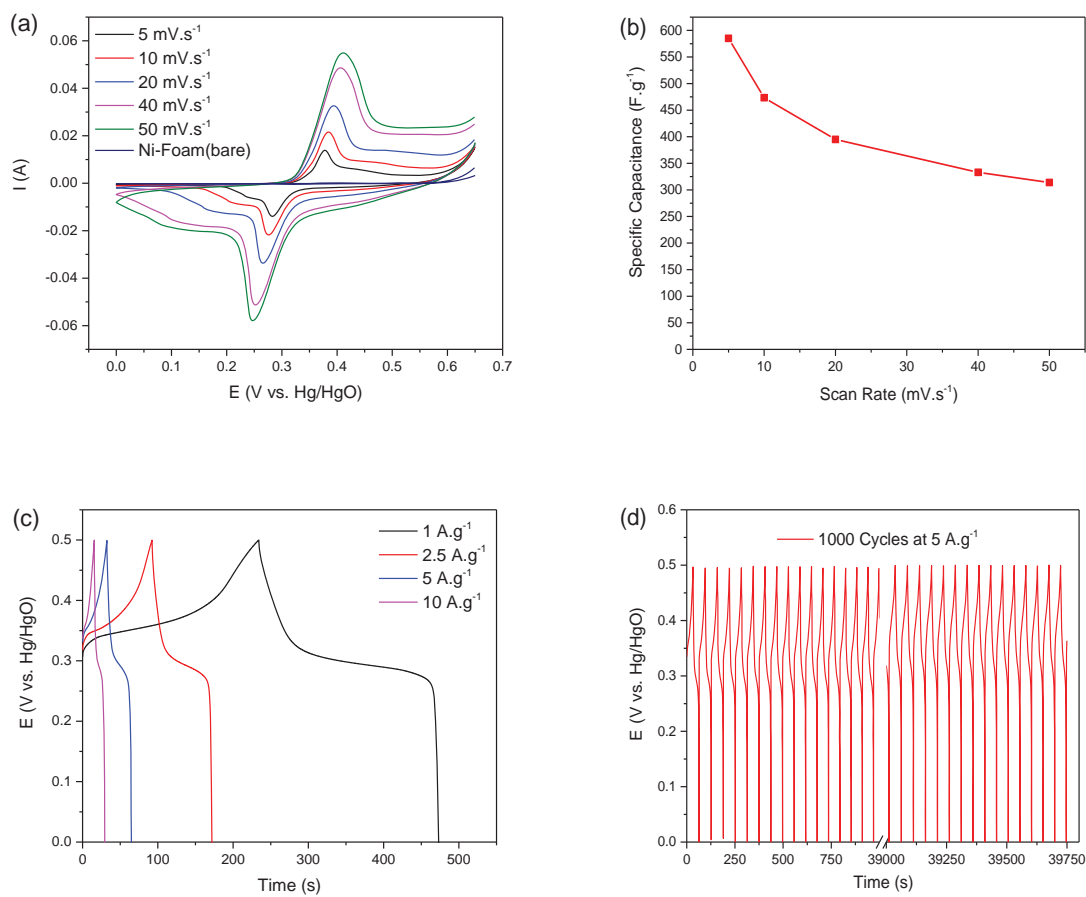


Figure 9 Supercapacitive properties of MnCo₂O₄/NGr. (a) CV of MnCo₂O₄/NGr loaded on nickel foam at different scan rates in 6M KOH with reference to the bare nickel foam. (b) Specific capacitance of MnCo₂O₄/NGr measured at different scan rates. (c) Charge-discharge curves of MnCo₂O₄/NGr at current densities of 1, 2.5, 5 and 10 A.g⁻¹, respectively. (d) Repeated 1000 charge-discharge cycles at 5 A.g⁻¹ on MnCo₂O₄/NGr loaded nickel foam.

Manganese cobalt oxide decorated carbon nanomaterial (MnCo₂O₄/NGr) displays excellent electrocatalytic and supercapacitive behavior. By combining the catalytic and pseudocapacitive characteristics of MnCo₂O₄, highly stable and efficient rechargeable Zn-air batteries are reported. Hybrid Zn-air battery benefits from this synergistic behavior and works at higher voltage and delivers more power density on discharge with more efficiency compared to conventional Zn-air battery.

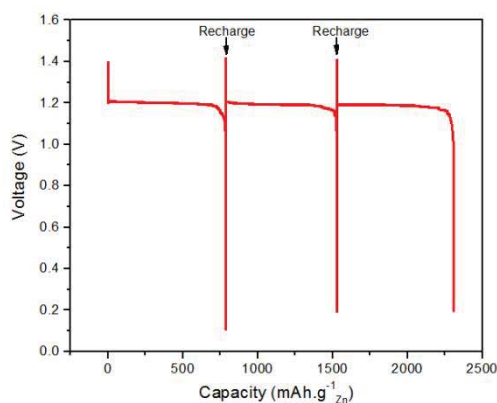
bifunctional catalyst, hydrothermal synthesis, primary zinc-air battery, hybrid zinc-air battery, supercapacitor.

Adnan Qaseem, Fuyi Chen*, Chuanzhou Qiu, Abdelaziz Mahmoudi, Xiaoqiang Wu, Xiaolu Wang and Roy L. Johnston*

Manganese Cobalt Oxide Decorated Reduced Graphene Oxide as Multifunctional Material for Mechanically Rechargeable and Hybrid Zinc Air Batteries

Rechargeable Zn-Air Battery

Mechanical



Hybrid

