Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

Augmented and sustained oxygen reduction reaction activity of $NiCo_2O_4$ by the incorporation of Ag

*Karuvatta Nubla †, Vadakkanethu Sadasivan Anju†, Aiswarya Sidharthan K#, and N. Sandhyarani†**

†Nanoscience Research Laboratory, School of Materials Science and Engineering, National Institute of Technology Calicut, Calicut, Kerala, India. * E-mail: sandhya@nitc.ac.in

#Department of Chemical Engineering, National Institute of Technology Calicut, Calicut, Kerala, India

S1: Synthesis of nickel oxide, cobalt oxide, and Ag/C

Synthesis of nickel oxide

0.75 g of nickel chloride was dispersed in 30 mL absolute ethanol under ultra-sonication for 10 minutes. 0.0126 M Sodium hydroxide in 25 mL ethanol was added dropwise to the nickel chloride solution and stirred for 1 hour. Obtained precipitate was washed with ethanol thrice and kept for drying at 105 ^{0}C for 3 hours in the oven. The synthesized nickel hydroxide was then calcined at 250 ^{0}C for 3 hours [1].

Synthesis of cobalt oxide

Cobalt oxide was synthesized by making slight changes in the reported literature [2]. 0.75 g of Cobalt nitrate and 0.5 g of sodium dodecyl sulfate (SDS) were dissolved in 20 mL absolute ethanol and an equal volume of water under ultra-sonication for 15 minutes resulting in an opaque lavender blush suspension. The obtained suspension was transferred to Teflon lined stainless steel autoclave and heated at 180 ^{0}C for 5 hours. The residue, which is lilaceous, was washed thoroughly with water and ethanol and dried. The obtained product (cobaltous carbonate) has been calcined at 250 ^{0}C for 3 hours to obtain cobalt oxide.

Synthesis of Ag/C

Ag/C was prepared as per a reported procedure after minor modifications. Briefly, 7 mL 0.1 M $AgNO_3$ solution was added to 20 mL 0.1M ammonia solution ($AgNO_3$/ammonia solution). 5 mg carbon black was added to 10 mL ethylene glycol and sonicated separately. The carbon black solution was then added to the $AgNO_3$/ammonia solution. 0.4 mL 1M NaOH solution was added to the mixture and stirred at 120 °C for 3 hours. Later, the mixture was centrifuged, washed with DI, and dried for 12 h [3].

S2: MEA preparation

Two sets of the membrane electrode assembly (MEA) were prepared, the first with Pt: Ru/C as anode catalyst and Pt/C as cathode catalyst, and the second with Pt: Ru/C and Ag-$NiCo_2O_4$ as anode and cathode catalysts, respectively. The gas diffusion layer (GDL) was prepared by ultrasonically mixing carbon black (4 mg/cm^2) in a 1:1 IPA/DI water mixture with a 5% Nafion binder. The slurry was then coated on PTFE (polytetrafluoroethylene) treated carbon cloth using a paintbrush. The catalyst inks for the anode and cathode were coated onto the previously arranged GDL using a paintbrush to load 3.5mg/cm^2 and 2 mg/cm^2 for the anode and cathode, respectively. After activating the Nafion 117 membrane in H_2O_2, H_2SO_4 followed by DI water; the MEAs were fabricated by inserting the pre-treated membrane between the anode and cathode catalyst through a hot-pressing process at 100°C and 76 kg/cm^2.

SEM images of Ag/C

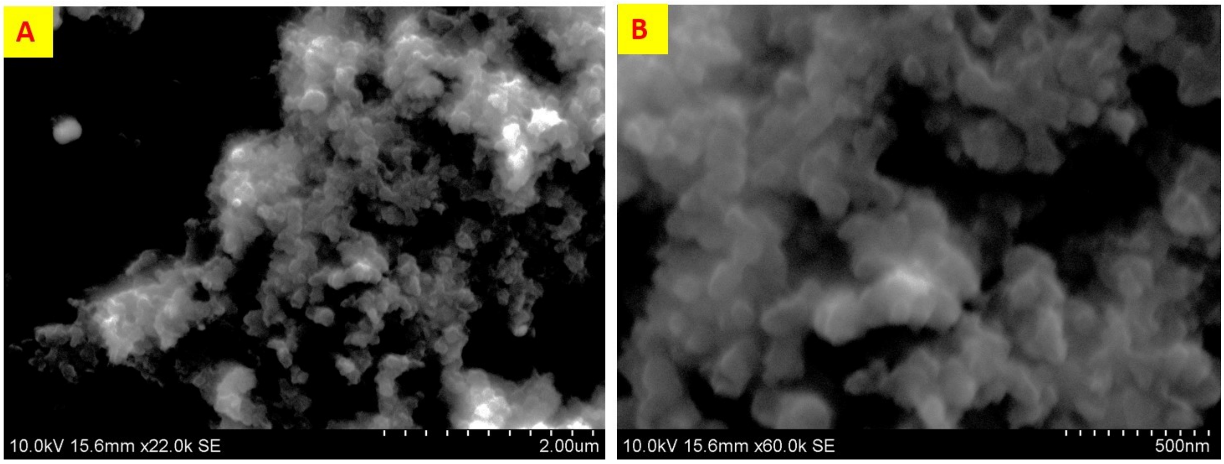

Figure S1: FE-SEM images of Ag/C (A and B)

XRD of Ag/C, NiO and Co_3O_4

The crystal structures of Ag/C, nickel oxide, and cobalt oxide were studied by X-ray diffraction technique and given in Figure S2.

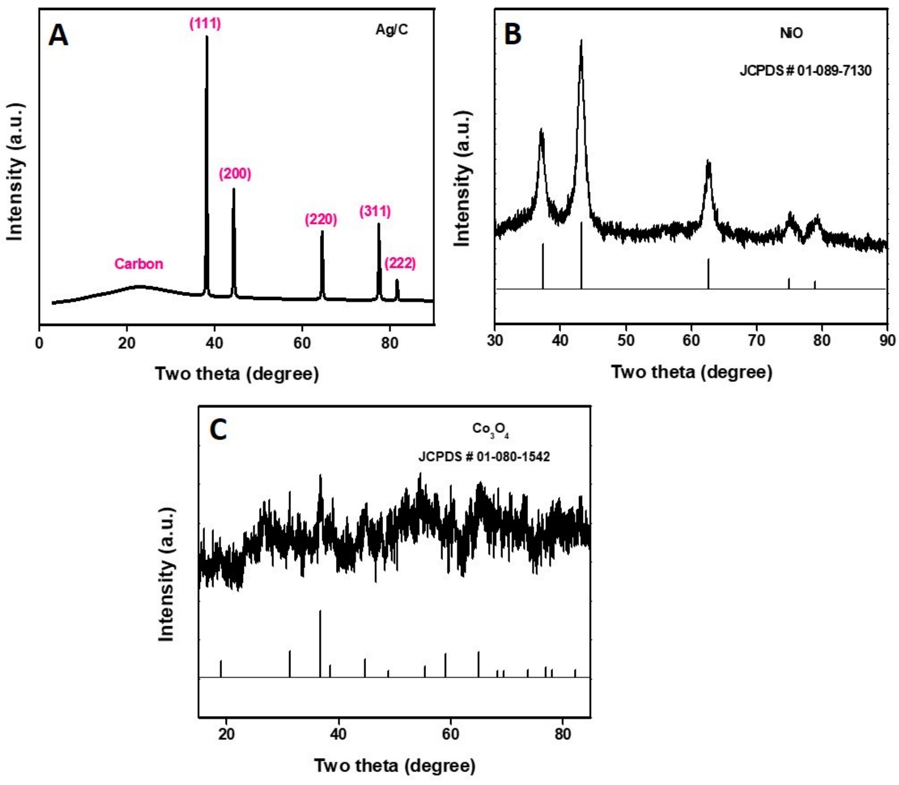

Figure S2: XRD pattern of (A) Ag/C (B) nickel oxide (C) cobalt oxide

The XRD spectrum of nickel oxide was displayed in Figure S2 (B). Well-resolved diffraction peaks at the two theta values of 37.07˚, 43.1˚, 62.5˚, 75˚, and 79˚ were observed, which are ascribed to the (111), (200), (220), (311), and (222) crystallographic planes of cubic nickel oxide (JCPDS#01-089-7130) [4,5]. XRD spectrum of cobalt oxide, given in Figure S2 (C), showed Bragg peaks at 18.9˚, 31.2˚, 36.8˚, 38.4˚, 44.6˚, and 65˚ are attributed to the (111), (220), (311), (222), (400) and (440) planes of cubic cobalt oxide (JCPDS#01-080-1542) [6,7].

LSV of NiO, Co_3O_4, Ag/C and commercial Pt/C

The electrochemical ORR performances of the synthesized nickel oxide, cobalt oxide, and Ag/C have been evaluated in O_2 saturated 0.1 M KOH solution.

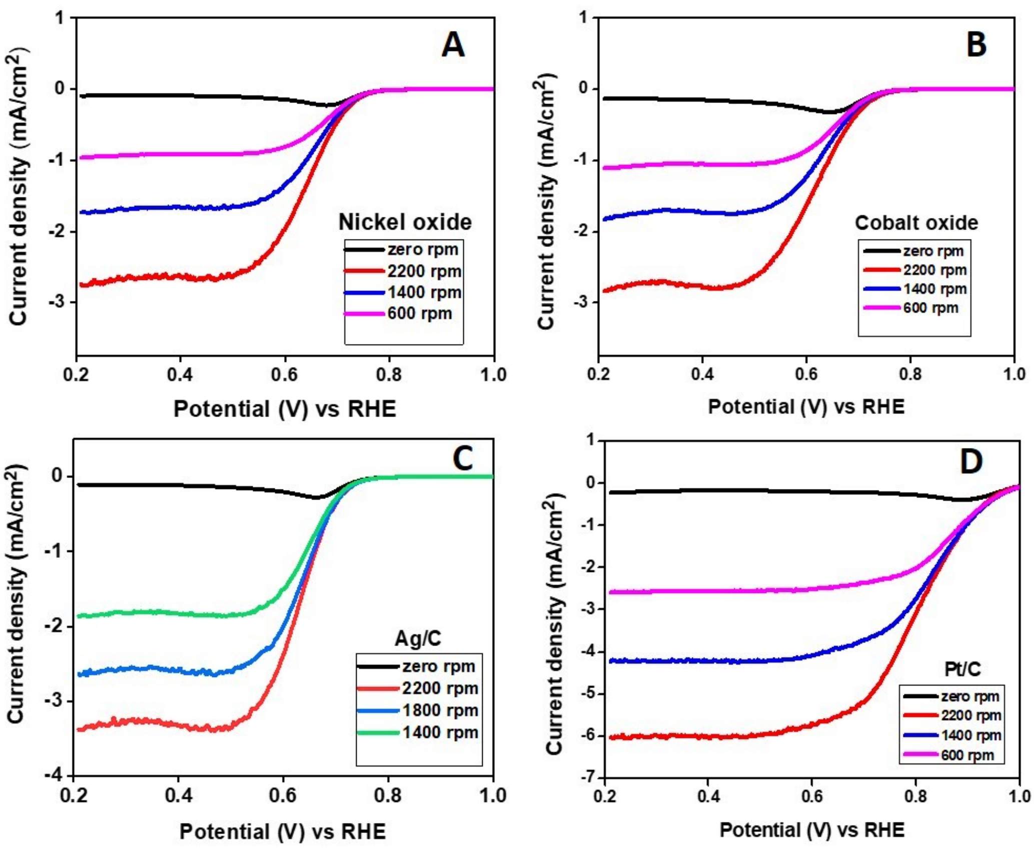

Figure S3: Linear sweep voltammogram at different RPM in O_2 saturated 0.1M KOH solution of (A) nickel oxide (B) cobalt oxide (C) Ag/C (D) commercial Pt/C

The LSV recorded at different electrode rotation rates is given in Figure S3 (A), (B), and (C), respectively. The LSV of the reference Pt/C is shown in Figure S3 (D).

Methanol tolerance and stability test-Ag/C at 1600 RPM

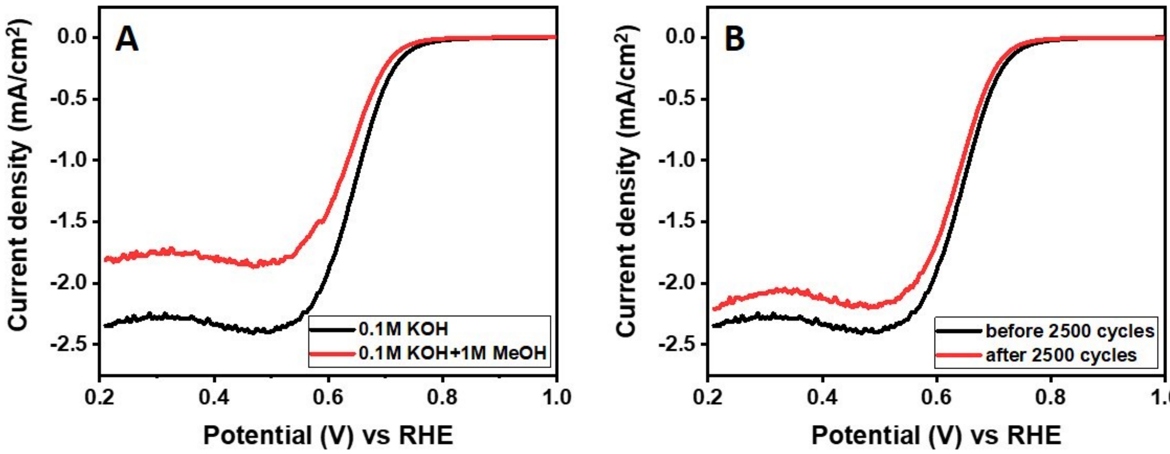

Figure S4: : Linear sweep voltammogram of Ag/C (A) before and after adding 1M methanol (B) before and after 2500 cycles of continuous CV scan in 0.1M O_2 saturated KOH.

To check the methanol tolerance of the Ag/C, LSV measurement has been performed @ 1600 RPM and shown in Figure S4 (A). After adding 1 M methanol, the ORR current density decreased to -1.8 mA/cm^2 (ΔI= 0.55 mA/cm^2). An accelerated durability test (ADT) was done to evaluate the stability of the Ag/C and the LSV plots before and after the 2500 continuous scan is given in Figure S4 (B). After 2500 cycles, the Ag/C exhibited a slight reduction in current density (ΔI =0.17 mA/cm^2).

Table S1: Comparison of the literature data for the ORR activity of various NiCo-based and Ag-based systems in O_2 saturated 0.1 M KOH electrolyte.

No.	Catalyst	Current density @1600 RPM in mA/cm^2	Onset potential (V)	Reference
1	Ag-$NiCo_2O_4$	-4.7	0.82 (vs RHE)	Present work
2	$NiCo_2S_4$/CNT	-2.66	0.84 V (vs RHE)	[8]
3	$NiCo_2O_4$/rGO	About -3.6	-	[9]
4	$NiCo_2S_4$/rGO	About -4.7	0.88 V (vs RHE)	[9]
5	$NiCo_2O_4$@PTL	-3.5	-	[10]
6	N-$NiCo_2O_4$@C	-5.2	0.9 V (vs RHE)	[10]
7	$NiCo_2O_4$/N-G	-5.27	0.90 V (vs RHE)	[11]
8	$NiCo_2O_4$/CNT	-4.84	About 0.81 V (vs RHE)	[12]
9	Co_3O_4-$NiCo_2O_4$/ N-rGO	-4.3	0.92 V (vs RHE)	[13]
10	$NiCo_2O_4$/CeO_2	-6.39	0.84 V (vs RHE)	[14]
11	(Ni,Co)S_2	-4.2	0.82 V (vs RHE)	[15]
12	$NiCo_2O_4$/N-CNF	-5.3	-	[16]
13	$NiCo_2O_4$/graphene	About -4.2	-0.12 V (vs SCE)	[17]
14	$NiCo_2S_4$@N/S-rGO	-4.3	-0.11 V (vs Ag/AgCl)	[18]
15	CeO_2/Ag	-5.33	0.96 V (vs RHE)	[19]

16	Mn_3O_4/Ag	-5.38	0.95 V (vs RHE)	[19]
17	Ag/MoS_2	-6.16	0.9 V (vs RHE)	[20]
18	Ag/$LaNiO_3$	-4.43	0.75 V (vs RHE)	[21]
19	GNP-Cu_3N/Ag	-4.86	0.904 V (vs RHE)	[22]

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