Supplementary Information (SI)

Electrochemical studies of non-aqueous Na-O_2 cells employing Ag-RGO as the bifunctional catalyst.

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Chemicals:

Graphite powder (Graphite India), $NaNO_3$, $KMnO_4$, KOH, Ethylene Glycol, $AgNO_3$ (all from S. D. Fine Chemicals), NaCl (Qualigens), $NaPF_6$ (Aldrich), poly vinylidene fluoride (PVDF, Aldrich), n-methyl pyrrolidinone (NMP, Aldrich), lithium ribbon (Aldrich) and tetraethyl glycol dimethyl ether (TEGDME, Aldrich) were used as received. Double-distilled water was used for all experiments.

Preparation of silver-reduced graphene oxide (Ag-RGO):

Ag-RGO is prepared by in-situ reduction of Ag^+ and graphene oxide by ethylene glycol, method already reported in our previous paper.[1] Graphite powder was converted into graphite oxide (GtO) by the procedure described by Hummers and Hoffeman.[2] Graphite oxide is converted to graphene oxide (GO) by ultra-sonication method. $AgNO_3$ (0.157 g) was dissolved in 100 ml double-distilled water and 100 mg GtO was added. The contents were sonicated for 15 min, and then 1M KOH while stirring the contents. 1M ethylene glycol was added to reduce both GtO and Ag^+ simultaneously while stirring the contents by a magnetic stirrer. The contents were kept at 80 ^{0}C and stirred for 3 h. The product of Ag decorated RGO was separated by

centrifugation, washed with double distilled water, and dried at 60 ^{0}C for 12 h. The mass ratio of Ag and RGO was 1:1.

Preparation of oxygen electrode for Na-O_2 cells:

For preparation of O_2 electrodes, method followed, is already reported in previous paper,[1] porous carbon paper (Toray) of 2.0 mm thickness was used as the current collector. One side of the carbon paper was coated with carbon diffusion layer and the other side with catalyst layer. High surface area carbon powder and PTFE suspension were mixed in 7:3 weight ratio. A minimum quantity of water was added to form dough, which was rolled into a layer. This layer was applied on one side of the carbon paper current collector. The Ag-RGO catalyst and PVDF were mixed (weight ratio: 92.5 : 7.5) in a mortar, a few drops of NMP were added to form an ink. The ink was coated on the other side of the carbon paper. The sandwich of diffusion layer, carbon paper and catalyst layer was pressed in a die at a pressure of 50 kN for 5 min. The electrode was dried at 100 ^{0}C for 12 h and transferred into an argon filled MBraun glove box model Unilab.[1] Na-O_2 cells were assembled in home-made Swagelok-type PTFE containers. The container had provision to close on one side where Na disk anode was placed and the other side open for exposure to oxygen gas from a cylinder. Stainless steel current collectors were used to take electrical contacts from the electrodes. The Na disk, a glass mat separator and the air electrode were sandwiched inside the PTFE container and stainless steel electric contacts were inserted and sealed. The glass mat was soaked in the electrolyte, which was made of 1.0 M $NaPF_6$ in TEGDME, before inserting into the cell. The catalyst layer of the O_2 electrode was exposed to the electrolyte and the diffusion-layer to oxygen gas.

Characterization of Ag-RGO:

A formation of Ag-RGO was analysed by powder XRD studies. The XRD pattern of Ag-RGO (Fig. SI 1a) consists of a broad reflection at 24.2^0 corresponding to the (002) plane of RGO and strong reflections at 2θ = 38.1, 44.3, 64.5 and 77.5^0, which are assigned to (111), (200), (220) and (311) planes, respectively, of face-centered cubic crystals of Ag (JCPDS file 04-0783). The crystallite size calculated from Ag(111) reflection using Scherrer's formula is 0.236 nm (2.36 Å).

TEM image of Ag-RGO sample are presented in Fig. SI 1b. The TEM images reveal the presence of layers of RGO and nanoparticles of Ag distributed uniformly on them. An analysis of particle size distribution, suggests the presence of Ag particles in 2-7 nm range.

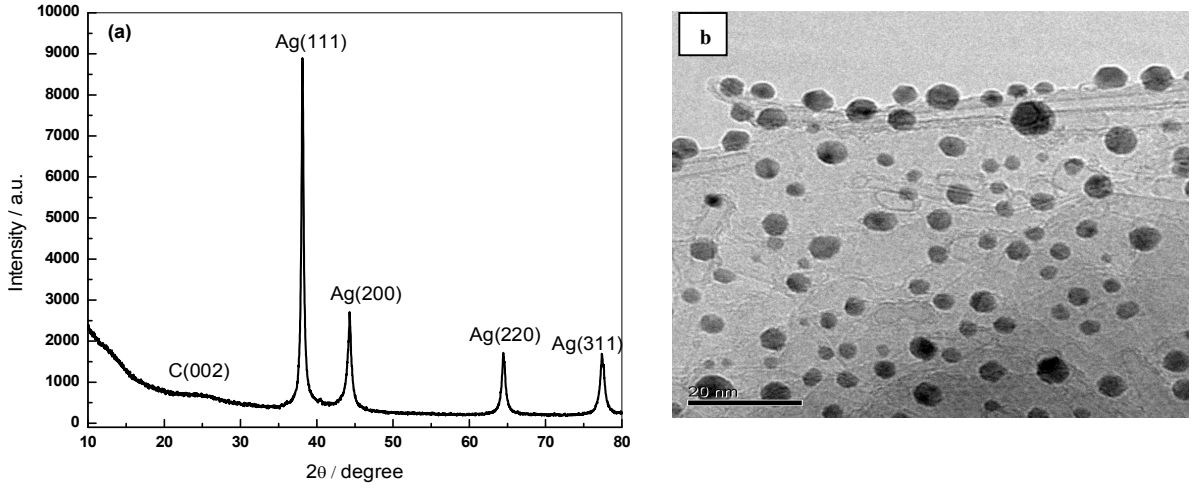


Fig. SI. 1. (a) Powder XRD pattern and (b) TEM image of Ag-RGO.[1]

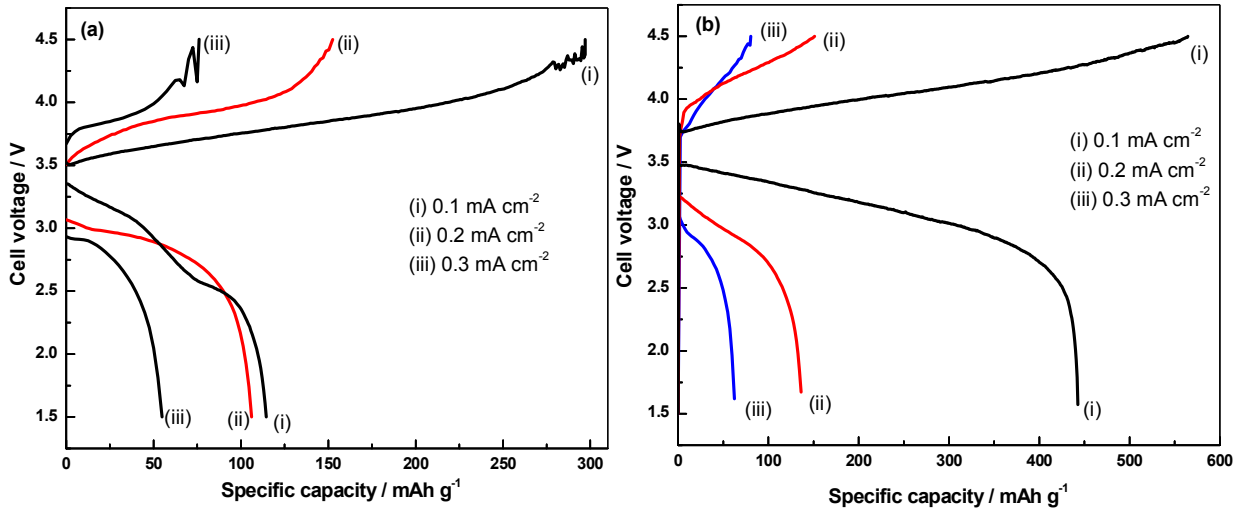
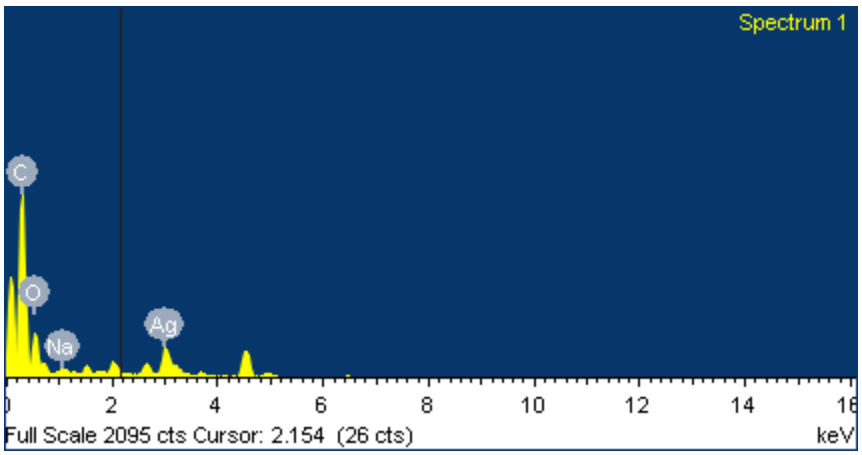
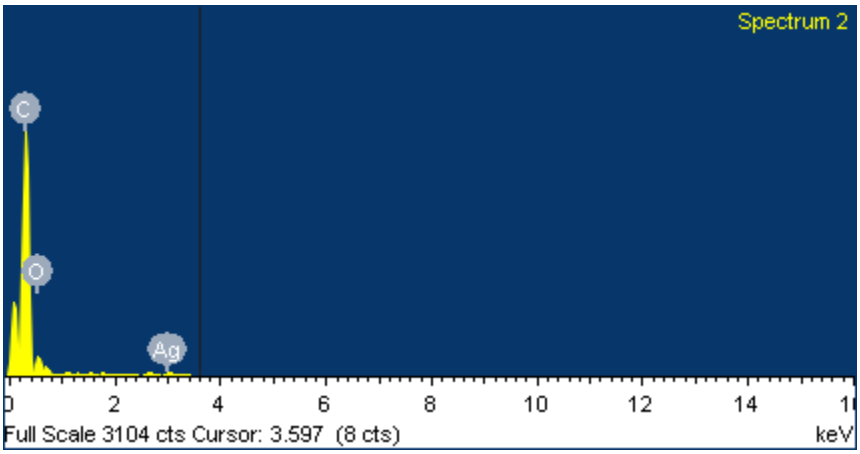


Fig. SI. 2. Charge-discharge profiles of Na-O_2 cells at the 1st (a) and 5th cycle at different currents.



Element	Weight%	Atomic%
C K	61.12	78.78
O K	18.29	17.70
Na K	1.08	0.73
Ag L	19.51	2.80
Total	100	

Fig. SI. 3. EXAD pattern of discharged oxygen electrode.



Element	Weight%	Atomic%
C K	60.78	85.05
O K	12.02	12.63
Ag L	27.19	2.32
Total	100	

Fig. SI. 4. EXAD pattern of charged oxygen electrode.

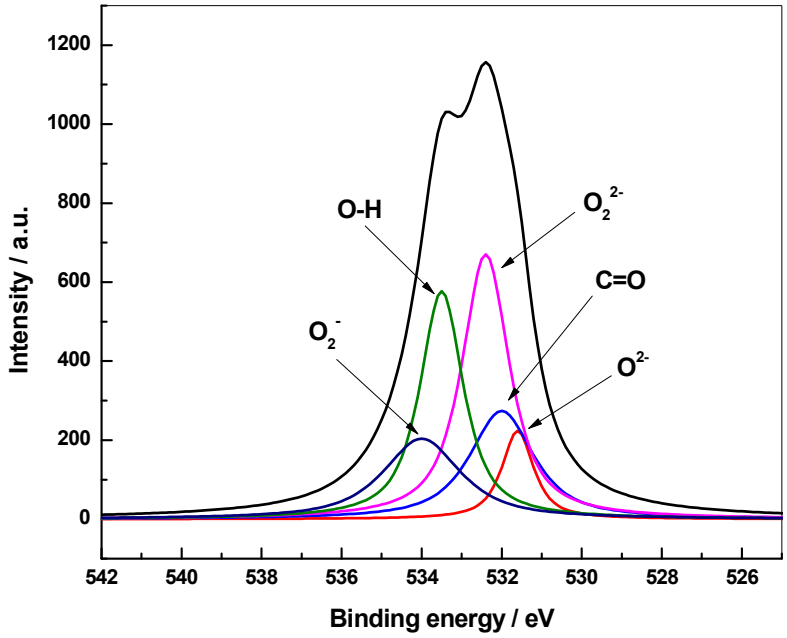


Fig. SI. 5. Deconvoluted XPS spectra of O 1s (full spectrum, discharged oxygen electrode).

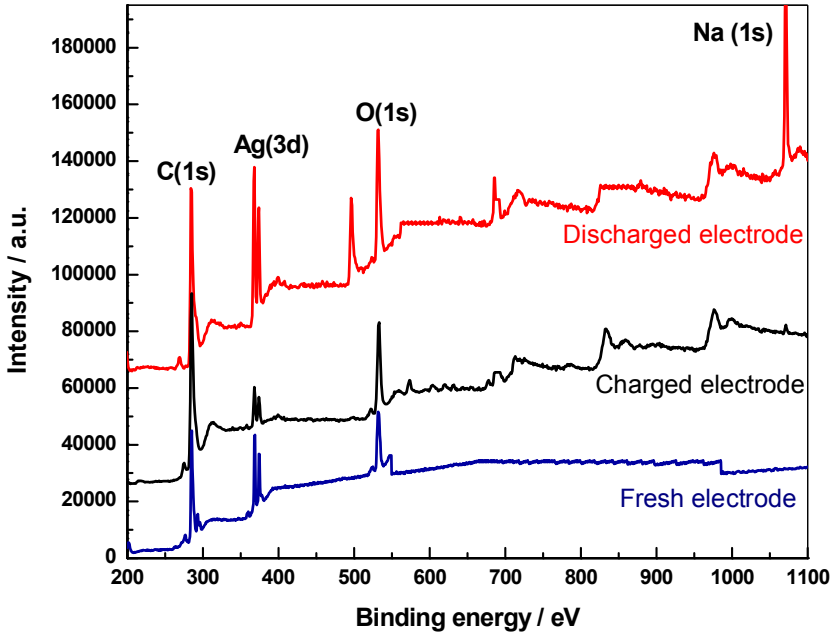


Fig. SI. 6. XPS spectra of the oxygen electrode of Na-O_2 cell.

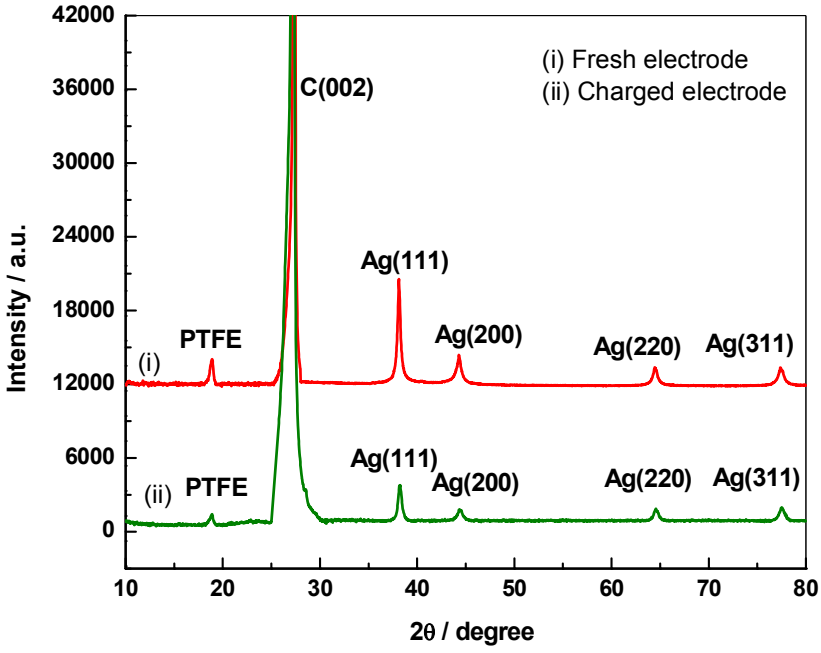


Fig. SI. 7. XRD pattern of the oxygen electrode of Na-O_2 cell.

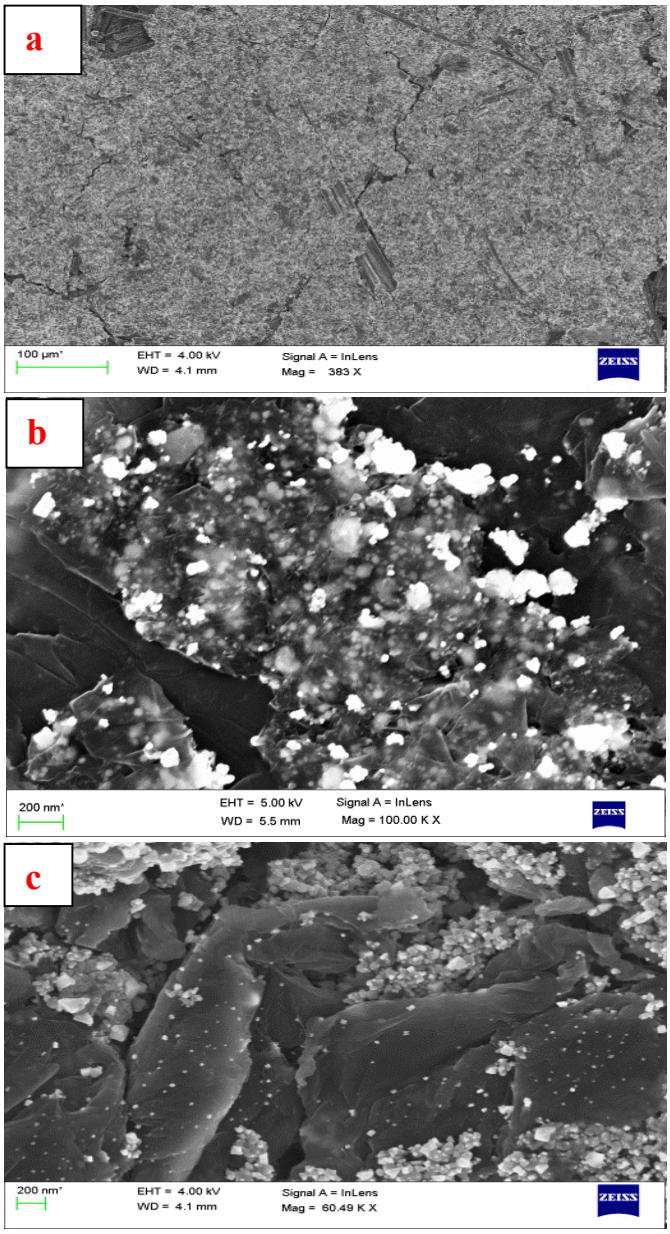


Fig. SI. 8. SEM images of fresh (a), discharged (b), and charged (c) oxygen electrode of Na-O_2 cell.

References:

[1] S. Kumar, C. Selvaraj, L. G. Scanlon and N. Munichandraiah, *Phys. Chem. Chem. Phys.* 2014, **16**, 22830 - 22840.

[2] W. S. H. Jr. and R. E. Offeman, *J. Am. Chem. Soc.* 1958, **80**, 1339.