Supplementary information (SI)

Nanoparticles of Pt_3Ni alloy on reduced graphene oxide (RGO) as an oxygen electrode catalyst in rechargeable Li-O_2 battery.

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1. Chemicals:

Graphite powder (Graphite India), $NaNO_3$, $KMnO_4$, KOH, $NaBH_4$, (all from S. D. Fine Chemicals), H_2PtCl_6, $NiCl_2$, NaCl (Qualigens), $LiPF_6$ (Aldrich), poly vinylidene fluoride (PVDF, Aldrich), n-methyl pyrrolidinone (NMP, Aldrich), lithium ribbon (Aldrich), tetrabutyl ammonium perchlorate (TBAP) and dimethyl sulphoxide (DMSO, Aldrich) were used as received. Double-distilled water was used for all experiments.

2. Raman spectroscopy

Raman spectra of RGO, Pt-RGO and Pt_3Ni-RGO are shown in Fig. SI.1. For all the samples, there are two bands. The band at 1358 cm^{-1} is assigned to the disorder induced D-band, while the band at 1613 cm^{-1} is to in-phase vibration of graphene lattice, i.e. G-band. The D-band originates from the defects present in graphene and it is expected to be absent in defect free graphene. Thus, it is inferred that the RGO samples possess significant defects. The G-band corresponds to the E_{2g} mode, which results from the vibration of sp^2 bonded carbon atoms. **The intensity ratio of D and G bands for RGO, Pt-RGO and Pt_3Ni-RGO are 0.94, 1.04 and 1.01 respectively.** These studies indicate that the spectrum properties of RGO undergo only minor changes on decorating with metals and alloys particles in the present work.

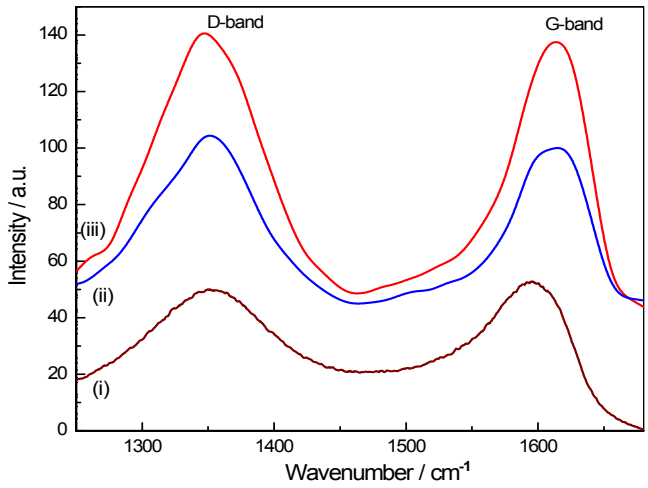

Fig. SI.1. Raman spectra of RGO (i), Pt-RGO (iii) and Pt_3Ni-RGO (iv).

3. XPS spectroscopy

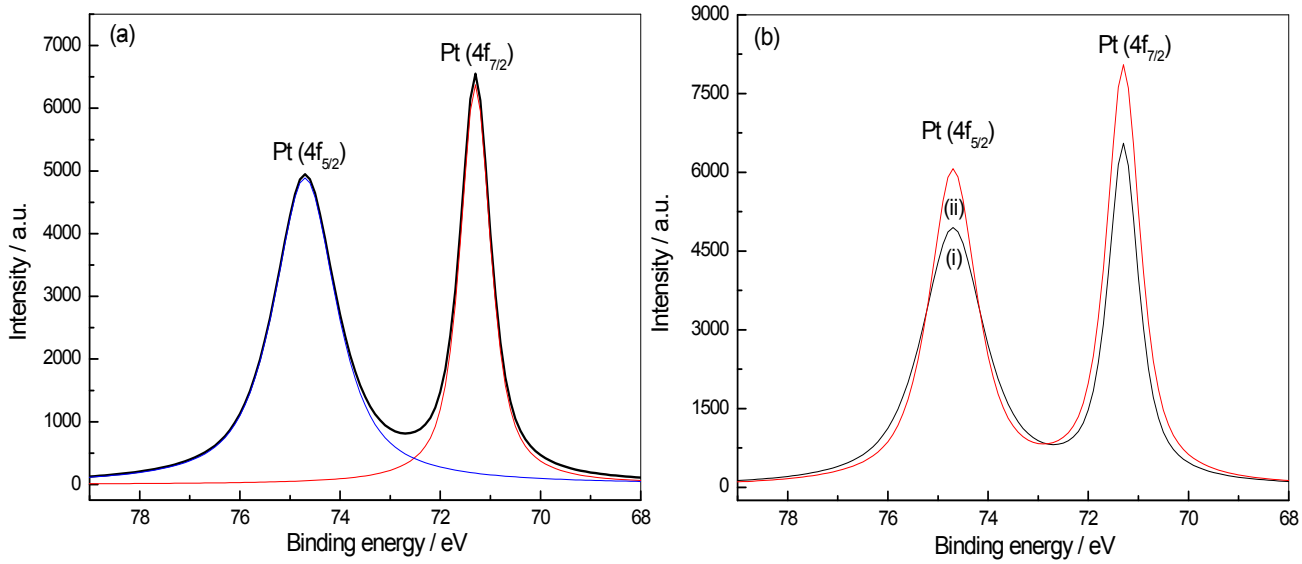

Fig. SI.2. (a) Deconvoluted XPS spectra of Pt 4f region and (b) comparison of 4f regions of Pt in Pt-RGO (i) and Pt_3Ni-RGO (ii).

In the survey spectrum of Pt-RGO signals corresponding to Pt 4p, 4d and 4f orbitals as well as C 1s and O 1s regions were present. In addition to these peaks, signals corresponding to Ni were present in Pt_3Ni-RGO. The XPS spectrum of Pt-RGO in the 4f region (Fig. SI.2a) consists

of a pair of peaks corresponding to Pt $4f_{7/2}$ at 71.3 eV and Pt $4f_{5/2}$ at 74.6 eV. Both these peaks are symmetrical and do not deconvoluted into additional peaks. Thus, they correspond to pure metallic Pt. The binding energy values agree with the literature report for Pt, where Pt $4f_{7/2}$ at 71.2 eV and Pt $4f_{5/2}$ at 74.5 eV are reported.[1] A comparison of Pt 4f regions of Pt-RGO and Pt_3Ni-RGO (Fig. SI.2b) suggest that both spectra are identical. Thus, it is inferred that the oxidation state of Pt is zero in both Pt-RGO and Pt_3Ni-RGO.

4. SEM and EDAX of Pt-RGO

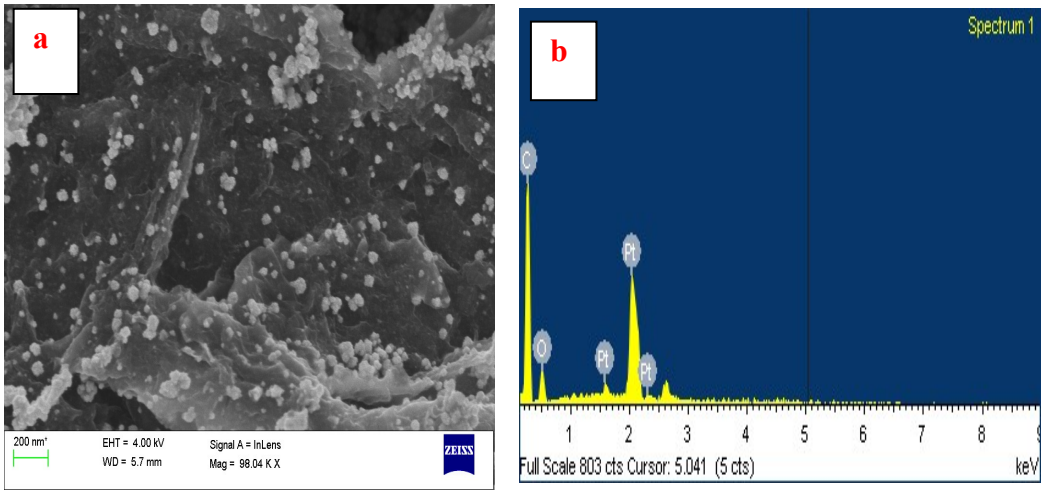

Fig. SI.3. SEM image (a) and EDAX pattern of Pt-RGO.

The morphology of Pt and Pt_3Ni nanoparticles are nearly same on graphene sheets, because of synthesis procedure was same. EDAX patterns of shows the presence of Pt, C and O elements in Pt-RGO sample.

5. Randle-Sevcik and Koutecky-Levich plots of Pt_3Ni-RGO

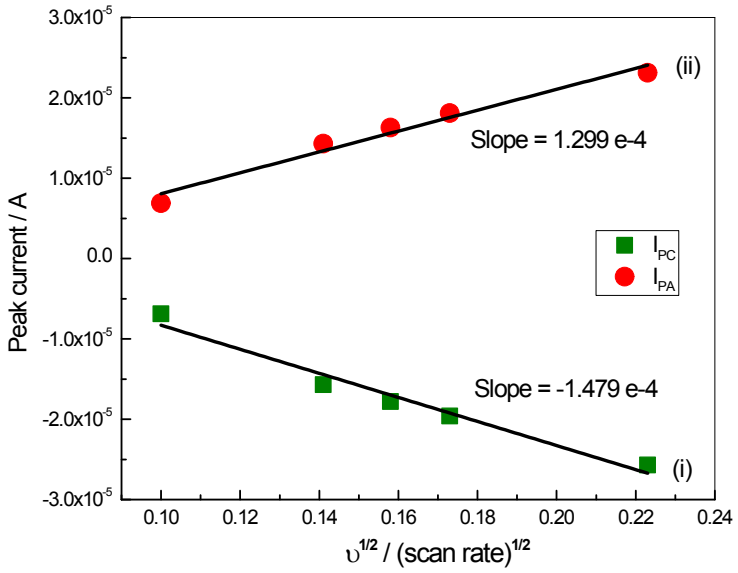

Fig. SI. 4. Plot between square root of scan rate and peak current.

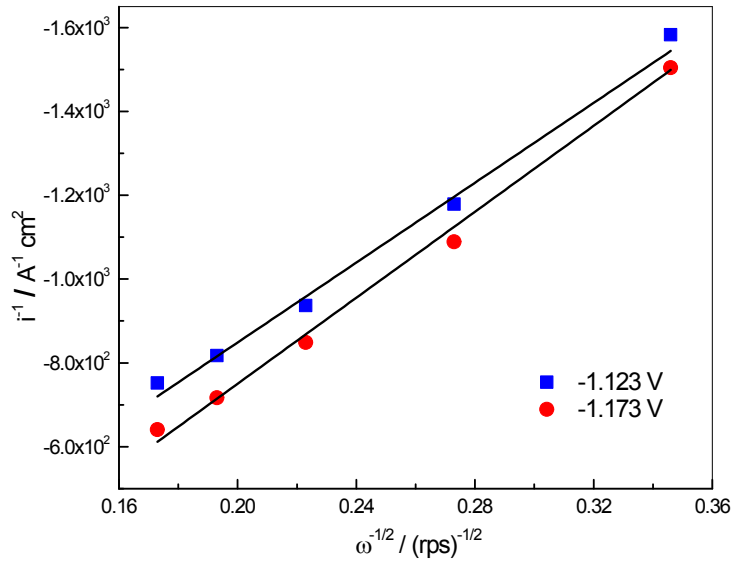

Fig. SI. 5. Koutecky-Levich plots at -1.123 and -1.173 V.

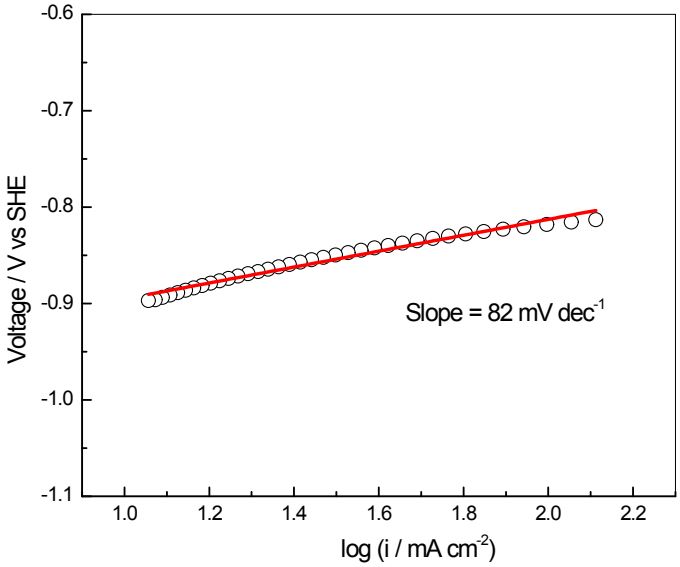

Fig. SI. 6. Tafel plot for ORR in 0.1 M TBAP-DMSO on Pt_3Ni-RGO.

6. ORR on Pt-RGO

CV of Pt-RGO coated GC electrode was recorded in O_2 saturated electrolyte 0.1 M TBAP in DMSO (**Fig. SI.** 7). Randles-Sevcik plot is shown in the Fig. **SI. 7b**.

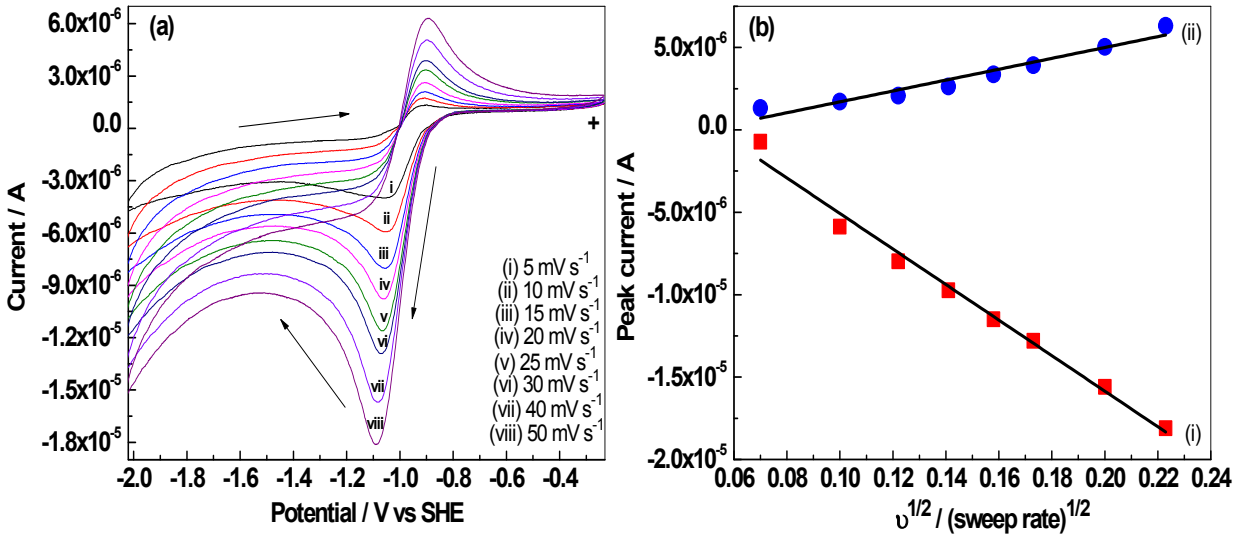

Fig. SI.7. (a) Cyclic voltammograms of Pt-RGO coated GC electrode at different scan rates and (b) plot between peak current versus (sweep rate)$^{1/2}$ for cathodic (i) and anodic peak (ii) in 0.1 M TBAP-DMSO electrolyte.

Linear sweep voltammogram recorded in O_2 saturated 0.1 M TBAP-DMSO solution at several speeds of RDE coated with Pt-RGO are presented in Fig. SI. 7. Levich and Koutecky-Levich plots are presented in Fig. SI. 7b and c. The values of diffusion coefficient and number of electrons obtained from the data are 1.6 x 10^{-6} cm^{-2} s^{-1} and 0.81, respectively.

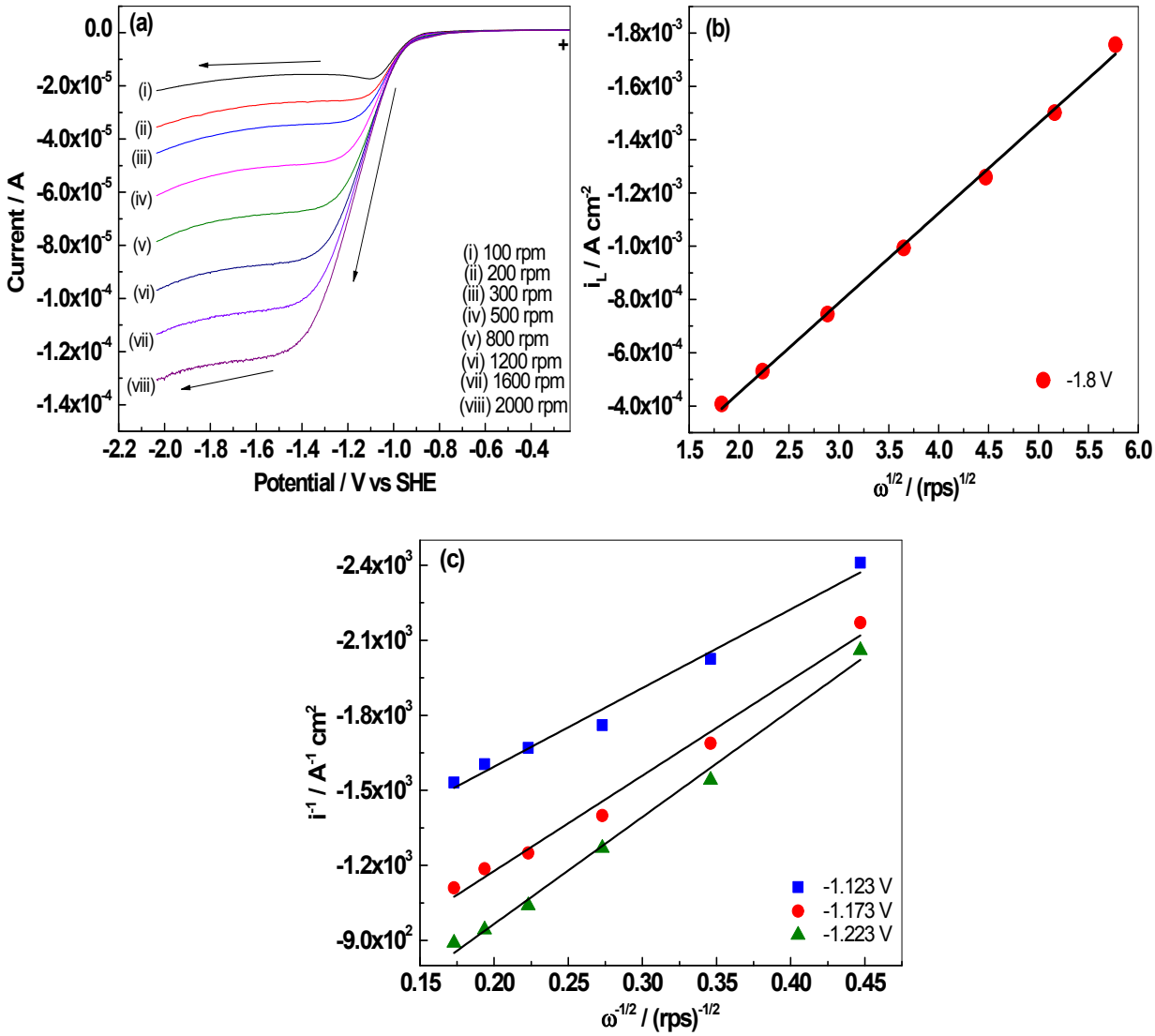

Fig. SI.8. (a) Linear sweep voltammetry of Pt-RGO coated GC electrode at 10 mV s^{-1} in O_2 saturated 0.1 M TBAP-DMSO at various speeds, (b) Levich plot and (c) Koutecky-Levich plot.

Reference: [1] D. Cahen and J. E. Lester, *Chem. Phys. Lett.*, 1973, **18**, 108 - 111.