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Pt and Pd Catalyzed Oxidation of Li_2O_2 and DMSO during Li-O_2 Battery Charging Supporting Information

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Experimental

Materials and Sample Preparation

H_2PtCl_6, $PdCl_2$, $LiClO_4$ and $HClO_4$ (99.999% trace metals basis) were purchased from Sigma-Aldrich. Anhydrous dimethyl sulfoxide (DMSO, <50 ppm water verified by Karl Fisher titration) was purchased from Alfa Aesar.

Pt and Pd porous electrodes were generated by applying an electroplating technique to flattened Ni foam substrates. All solutions for electroplating were prepared with Milli-Q water. Ni foam substrates (12.7 mm diameter) were immersed in solutions of 5 mM $PdCl_2$ or H_2PtCl_6 in 0.1 M $HClO_4$. Constant currents of 100 µA or 1000 µA were applied cathodically to the Ni foam substrate over 5 min for Pt and Pt deposition, respectively. A Pt mesh counter electrode and Ag/AgCl reference electrode were used. Coulometrically calculated masses of Pd and Pt deposited are 17 µg and 152 µg per electrode, respectively. Electrodes were removed from salt solutions, rinsed thoroughly with DI water and dried at 100 °C.

Cell Assembly

Li-O_2 cells were assembled inside an argon purged glovebox using an in-house design described elsewhere.[1] A piece of 11.1 mm diameter Li foil was used as the counter electrode with a 13 mm diameter Whatman glass fiber separator (GF/A). The separator was impregnated with 60 µL of 0.1 M $LiClO_4$/DMSO. Sealed cells were removed from the glovebox, purged several times with dry O_2 and resealed prior to cycling.

Electrochemical Characterization

A BioLogic VSP potentiostat was used for the galvanostatic cycling of cells and cyclic voltammetry. Galvanostatic discharge of electrodes was conducted with a rate of 40 $\mu A/cm^2_{geometric}$ from open circuit potential to 2.0 V vs. Li/Li^+. Afterward, cell charging was conducted using a staircase sequence every 0.1 V (held for 15 min) from 3.0 to 4.0 V.

Physical Characterization

Microscopy of Pd and Pt electrodes was conducted with a Hitachi SU-70 scanning electron microscope (SEM). A Bruker D8 Focus X-ray diffractometer (XRD) was used to evaluate Pt and Pd electrode crystallinity. *Ex situ* Raman spectroscopy of galvanostatically cycled electrodes used a Horiba Jobin-Yvon T64000 Raman spectrometer with a 633 nm excitation wavelength. Spectra for these *ex situ* samples were averaged over 30 min. X-ray photoelectron spectroscopy (XPS) measurements were performed at Brookhaven National Laboratory on a SPECS GmbH instrument under ultrahigh vacuum (UHV) conditions. The X-ray source was Al Kα at a power of 300 W. Data were collected for C 1s, O 1s, Pt 4f, Pd 3d and Li 1s with a pass energy of 25 eV.

Sample binding energies were calibrated to either the C 1s photoemission peak of adventitious hydrocarbons (C-H) at 285.0 eV or the carbonate (CO_3^{2-}) feature at 290.0 eV. Peak locations and peak widths were obtained using a Shirley background subtraction and by fitting the data to mixed Gaussian−Lorentzian line shapes (CasaXPS).

In Situ Raman Spectroscopy

The *in situ* Li-O_2 optical cell had the same structure as cells used for other cycling experiments except for the addition of a 0.4 mm thick sapphire window (Edmund Optics) at the center of the anode current collector.[2] Small holes were cut in the Li foil anode and separator to allow an optical path to the oxygen electrode surface. The in-cell optical path length was ∼1 mm. *In situ* Raman spectroscopy was conducted using a Jasco 3100 laser Raman spectrophotometer with a 785 nm excitation wavelength. *In situ* spectra were measured following discharge at voltage steps of 0.05 V from 3.0 to 4.0 V for the charge, each over 3 min (six 30 sec accumulations). The intensity of the DMSO feature at 673 cm^{-1} was normalized for all spectra to the Raman intensity at 1250 cm^{-1}, where no features are expected.

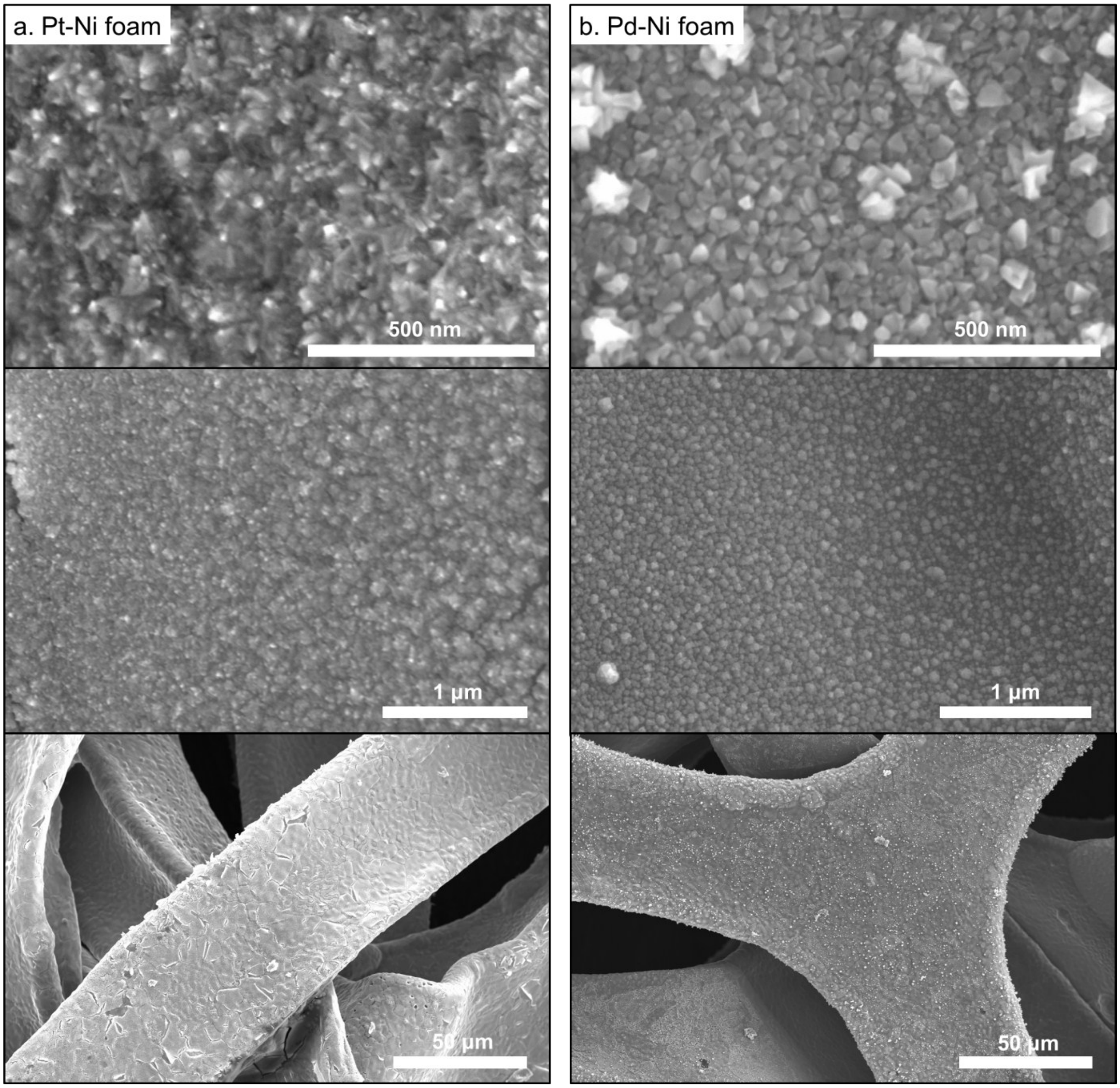

Figure S1 SEM images of (a) Pt-Ni foam and (b) Pd-Ni foam electrode surfaces collected at different magnifications.

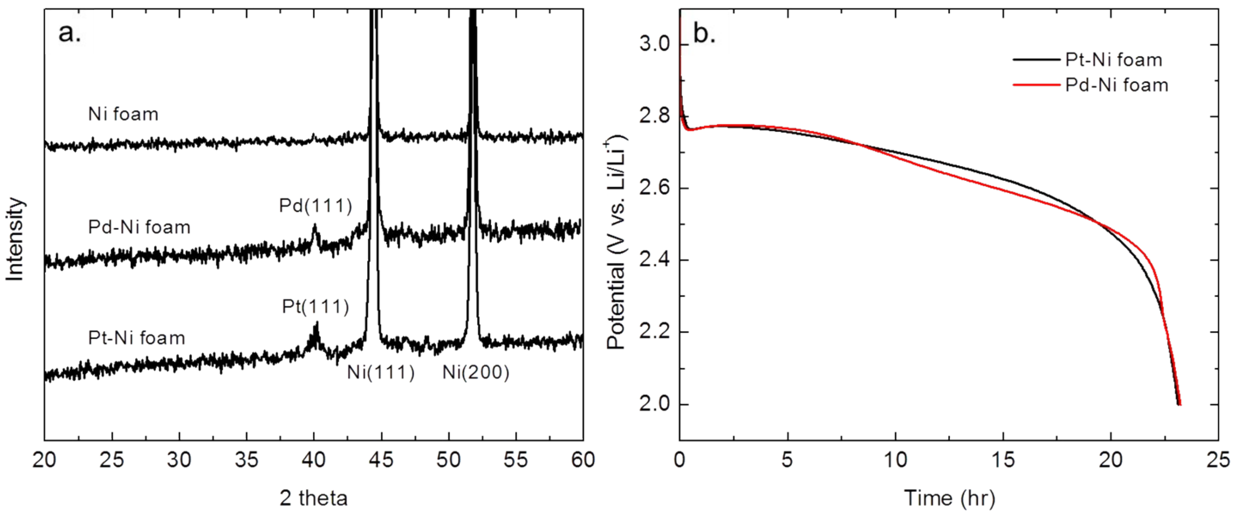

Figure S2 (a) Diffraction pattern of electrodes before and after Pt or Pd electrodeposition, (b) discharge profiles of typical Pt-Ni foam and Pd-Ni foam electrodes.

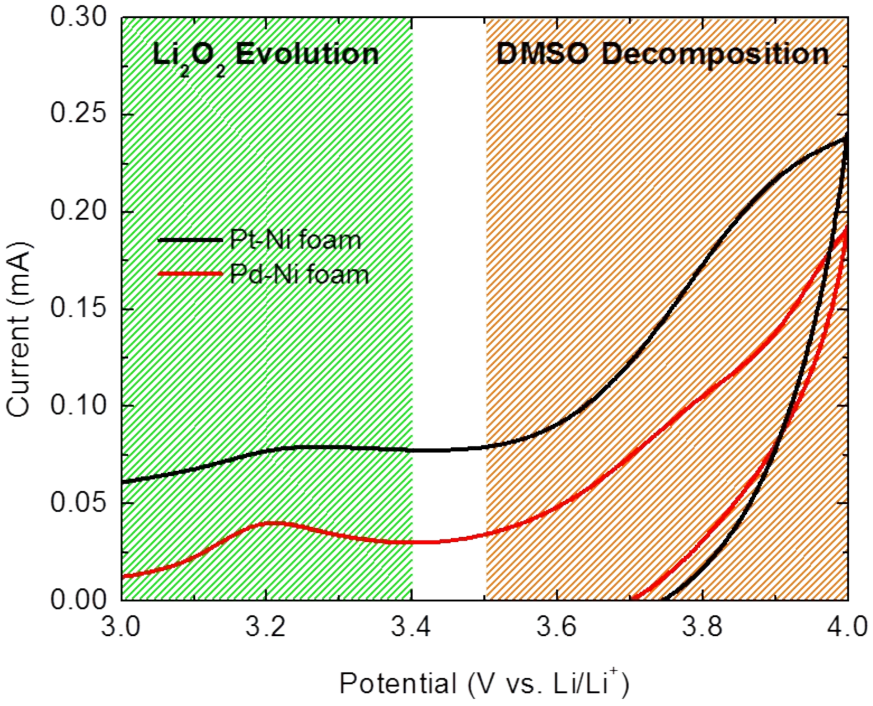

Figure S3 Cyclic voltammogram charge region of Li-O_2 cells with Pt and Pd electrodes, cycled at 5 mV/s.

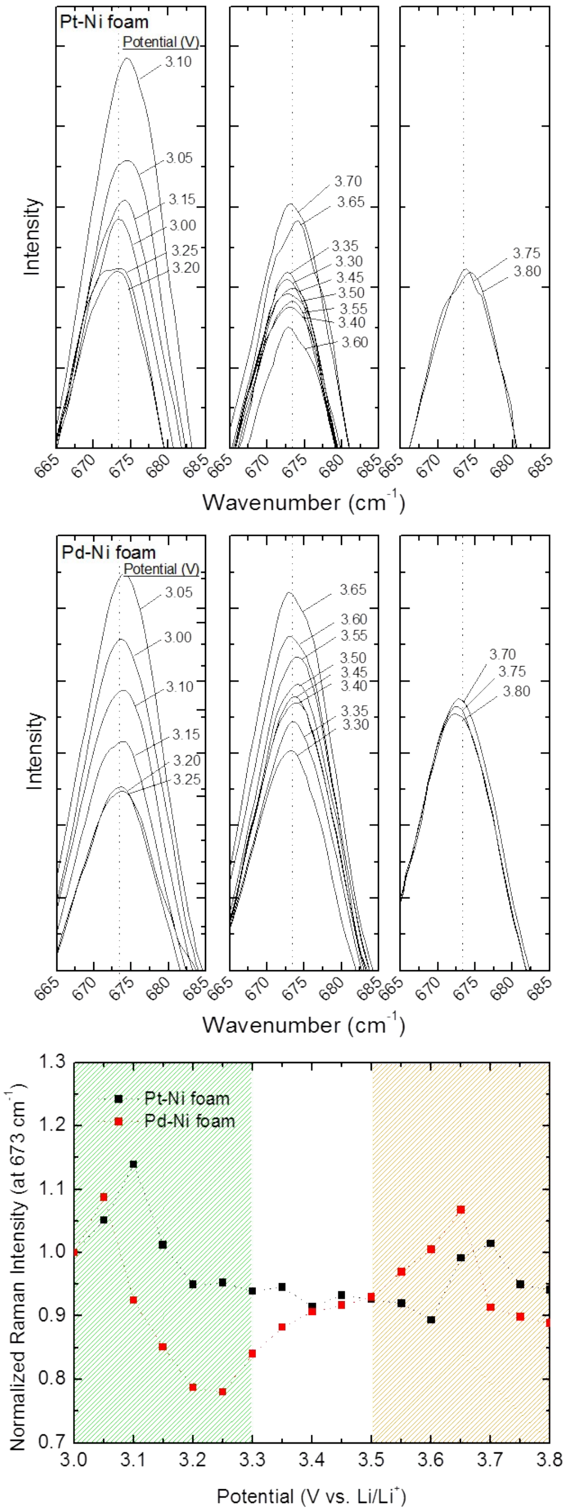

Figure S4 *In situ* Raman spectral intensity of a DMSO feature (C-S antisymmetric stretch) near the Pt and Pd electrode surface at various applied charge potentials. Increases in feature intensity correspond to processes at which DMSO molecules are closer to the surface – due to evolution of Li_2O_2 solid products at low potentials or DMSO oxidative decomposition at high potentials.

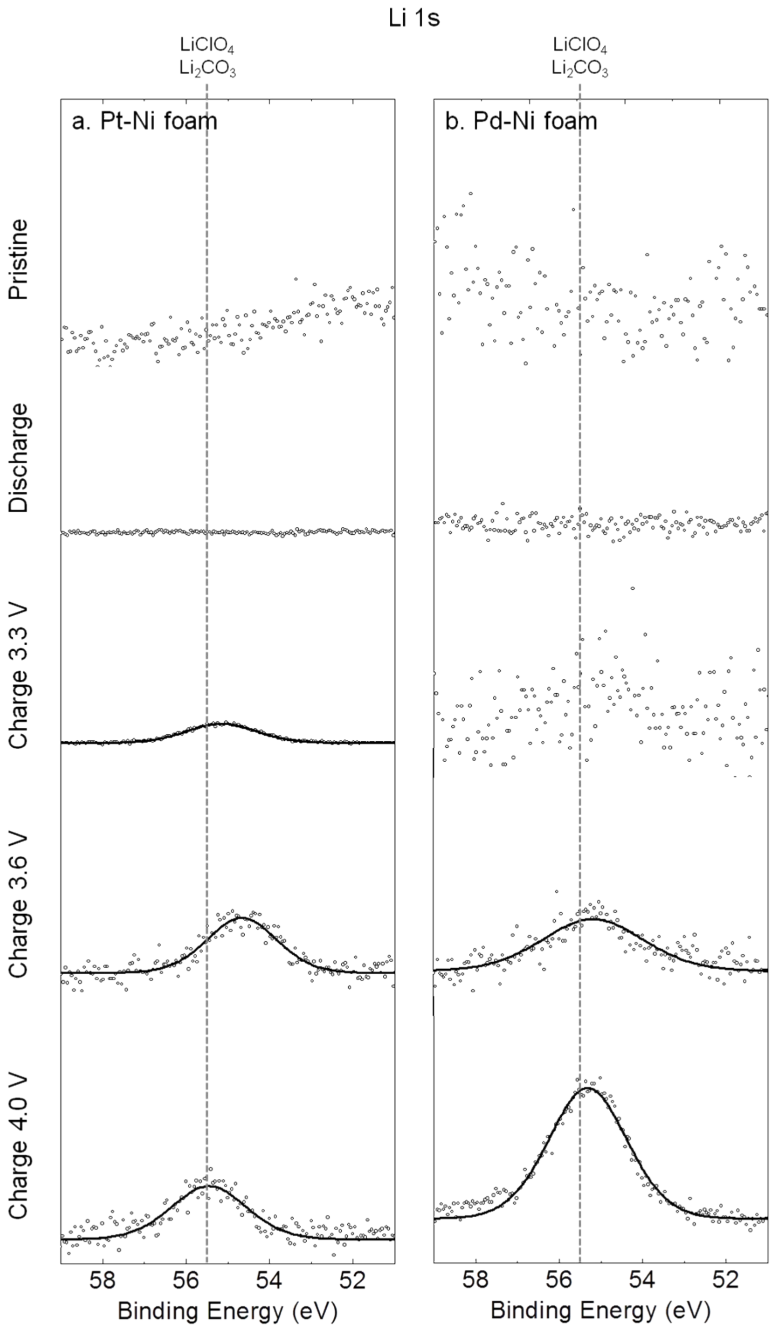

Figure S5 *Ex situ* Li 1s X-ray photoelectron spectra of Pt-Ni foam and Pd-Ni foam electrodes at various states of charge. An increase in Li features correlates with the growth of Li_2CO_3 during charging.

References

1 F. S. Gittleson, R. C. Sekol, G. Doubek, M. Linardi and A. D. Taylor, *Phys. Chem. Chem. Phys.*, 2014, **16**, 3230–3237.

2 F. S. Gittleson, W. Ryu and A. D. Taylor, *ACS Appl. Mater. Interfaces*, 2014, **6**, 19017–19025.