Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Catalyst and Electrolyte Synergy in Li-O_2 Batteries
Supporting Information

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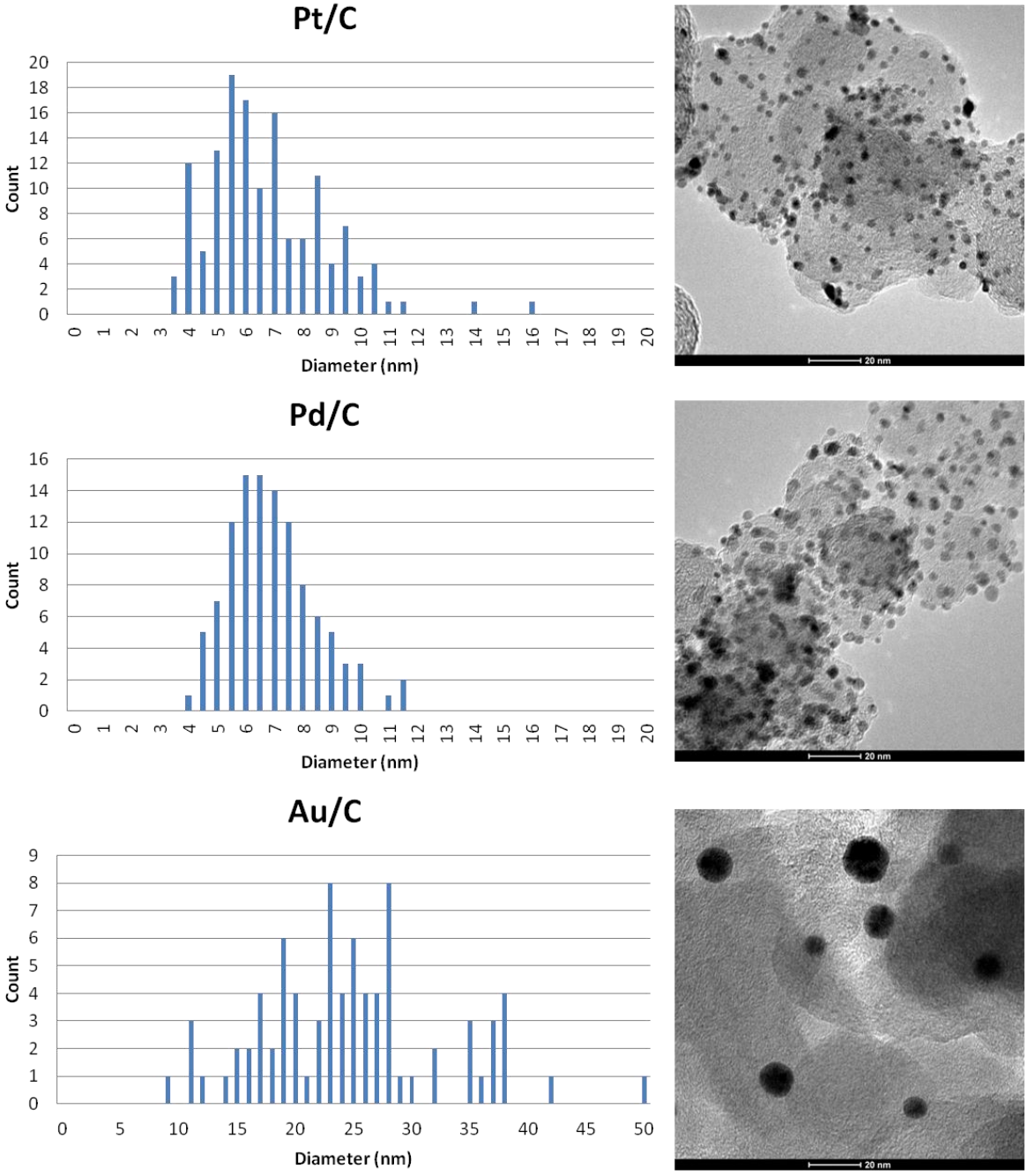

Fig. S1 Particle size distributions of supported noble metal catalysts from TEM analysis with sample TEM images alongside. Pt and Pd particles have an average diameter of 6.5 nm and 6.7 nm, respectively, while Au particles have an average diameter of 25 nm.

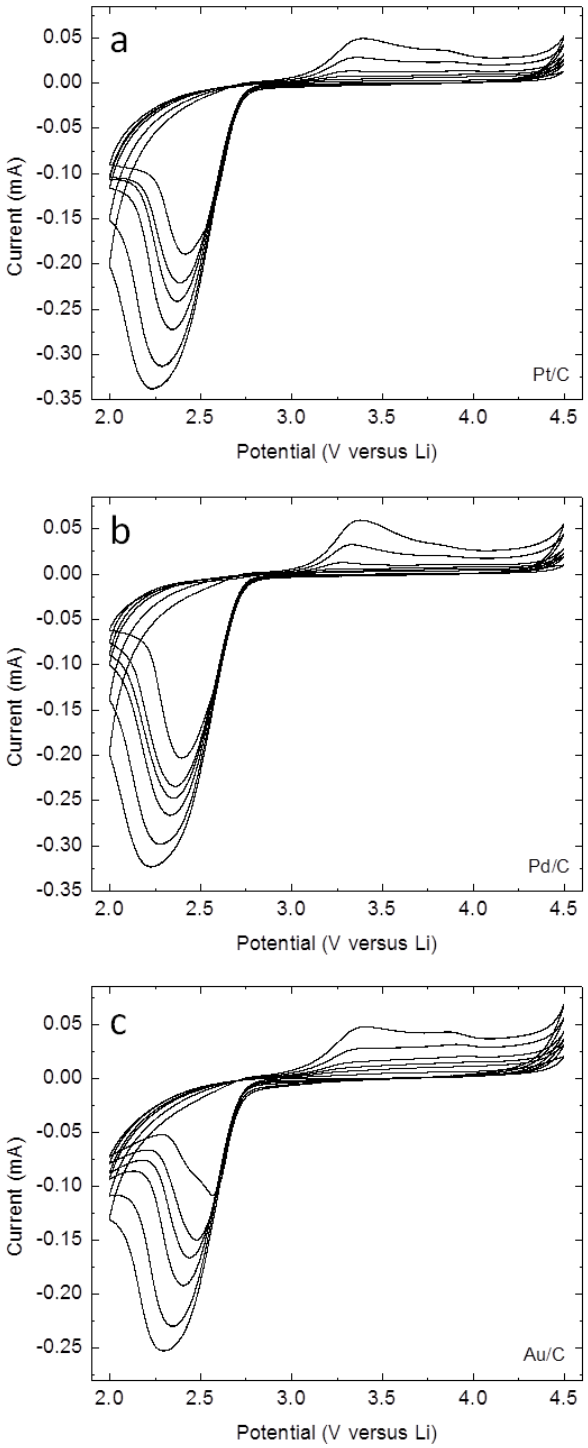

Fig. S2 CV of glassy carbon electrode with (a) Pt/C, (b) Pd/C and (c) Au/C at increasing scan rates 1, 5, 10, 20, 50, 100 mV/s in a DMSO-based electrolyte under O_2 atmosphere. Carbon black baseline available in Fig. 1 of the text.

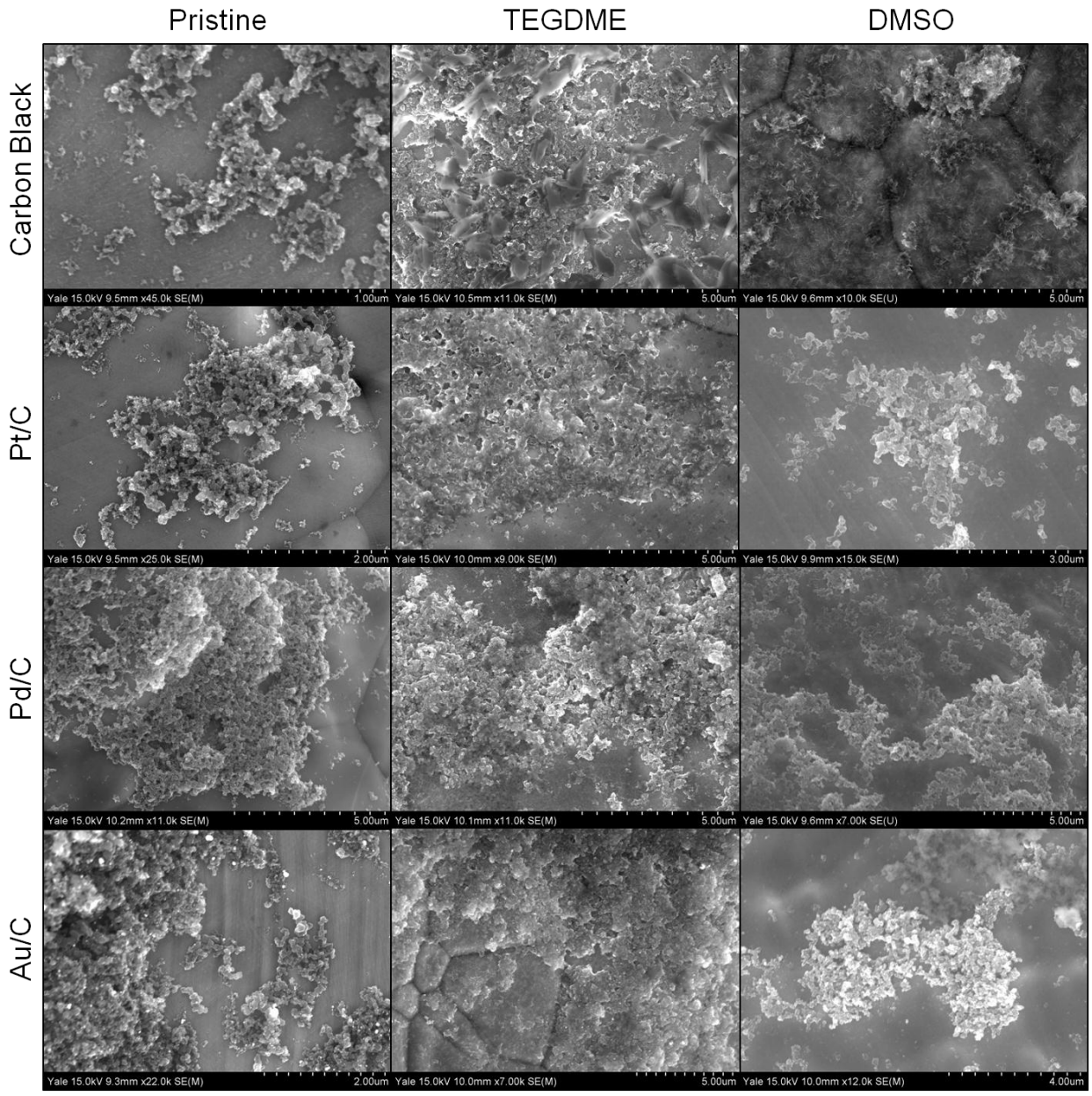

Fig. S3 SEM images of carbon support on Ni-foam before and after 20 cycles in TEGDME and DMSO electrolytes.

Properties of Electrolyte Solvents	DME	TEGDME	DMSO
Oxygen solubility (mM)	9.57	4.43	2.1
Viscosity (cP)	0.46	4.05	1.948
Donor number (kcal/mol)	20	16.6	29.8
Diffusion coefficient with Li^+ (cm^2/s)	1.22×10^{-5}	2.17×10^{-6}	1.67×10^{-5}
Conductivity of Li^+ (mS/cm)	1.16	0.3	2.11

Table S1 Summary of electrolyte solvent properties, reproduced from Laoire et al.[1]

Tafel Analysis

The following analysis was applied to the data shown in Fig. 3d-f of the text for the reduction reaction in the second cycle. Following the method of analysis in Laoire et al.[1], exchange current density, Tafel slope and corresponding charge transfer coefficients were calculated using an overpotential range from -0.2 to -0.3 for the reduction reaction. Results indicate that the exchange current density is similar across the three electrolytes, with DME exhibiting a slightly higher current density for all catalysts. Pt/C and Pd/C exhibit higher exchange current densities than Au/C in all electrolytes. Kinetic differentiation among electrolytes can be observed in the lower Tafel slopes and higher charge transfer coefficients with DMSO vs. DME and TEGDME. Based on the theoretical meaning of the charge transfer coefficient, α, catalysts in DMSO exhibit a lower free energy barrier to the electrochemical formation of the superoxide (the limiting one electron reaction, discussed in the text). The kinetic synergy of Pt/C and Pd/C with DMSO is jointly explained by higher exchange current densities (vs. Au/C) and improved charge transfer with a DMSO electrolyte.

We note that Tafel analysis only applies to reversible reactions, of which oxygen reduction to Li_2O_2 is not. The first step of the generally accepted mechanism involving the formation of the superoxide may be reversible, but distinguishing between the onset of each intermediate reaction is especially difficult and can be confounded by the Tafel fitting. Thus, Tafel analysis in this case must be taken with a grain of salt.

Exchange Current Density (mA/cm^2)	DME	TEGDME	DMSO
Pt/C	0.0620	0.0471	0.0467
Pd/C	0.0602	0.0403	0.0388
Au/C	0.0293	0.0181	0.0145

Table S2

Tafel Slope (mV/dec)	DME	TEGDME	DMSO
Pt/C	462	536	127
Pd/C	453	431	138
Au/C	894	406	90

Table S3

Charge Transfer Coefficient, α	DME	TEGDME	DMSO
Pt/C	0.06	0.05	0.20
Pd/C	0.06	0.06	0.19
Au/C	0.03	0.06	0.29

Table S4

Cycle 20 Discharge Capacity ($mAh/g_{catalyst/C}$)	TEGDME	DMSO
Carbon Black	40.5	175.4
Pt/C	144.1	351.1
Pd/C	78.8	707.4
Au/C	51.9	406.0

Table S5 Discharge capacity values of cycle 20 from Fig. 6 in the text.

References

1. C. O. Laoire, S. Mukerjee, K. M. Abraham, E. J. Plichta, and M. A. Hendrickson, *J. Phys. Chem. C*, 2010, **114**, 9178–9186.