Electronic Supplementary Information (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Mechanistic Origin of Low Polarization in Aprotic Na-O₂ Batteries

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Additional experimental methods

UV-Vis spectroscopy.

UV-Vis spectroscopy (UV-2600, SHIMADZU) was carried out to determine the K_{sp} of NaO$_2$ in DMSO. To measure K_{sp}, the molar absorption coefficient (ε) of O$_2^-$ in DMSO was first determined. Briefly, stock solutions of 0.1, 0.3 and 0.6 mM TMAO$_2$ DMSO were prepared in an Ar filled glove box. UV-Vis spectra of the stock solutions with known O$_2^-$ concentration were collected and used to determine the ε (Figure S3a) based on the Lambert-Beer law. The K_{sp} of NaO$_2$ in DMSO was then obtained by measuring the UV-Vis spectrum of diluted solutions of NaO$_2$-saturated DMSO (Figure S3b). The concentration (C_1) of NaO$_2$-saturated DMSO was calculated based on the acquired ε (Figure S3a) and the absorbance of 100 times diluted solution Figure S3b. Thus, C_1 (saturated-NaO$_2$) =100×C (diluted-100) =100×0.266×10^{-3} mol/L =2.66×10^{-2} mol/L. Similarly, C_2 (saturated-NaO$_2$)=50×C (diluted-50)=50×0.578×10^{-3} mol/L=2.98×10^{-2} mol/L. Since the values of NaO$_2$-saturated C_1 and C_2 were close, the K_{sp} of NaO$_2$ in DMSO was K_{sp} = [(2.66×10^{-2}+2.98×10^{-2})/2]^2 = 7.95×10^{-4}.
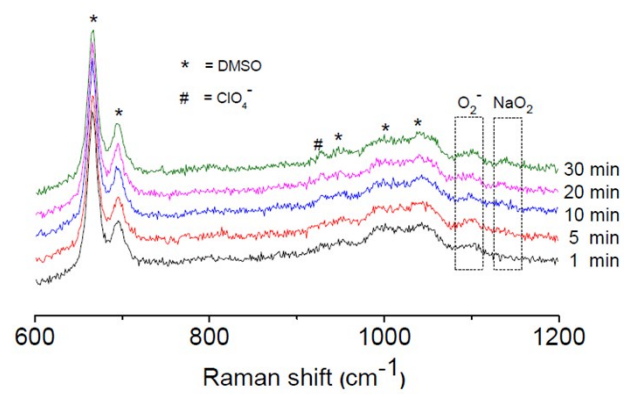
Figure S1. SERS spectra collected on an Au electrode polarized at 1.94 V (*vs.* Na/Na$^+$) in an O$_2$ saturated 0.1 M NaClO$_4$ DMSO solution as a function of time.
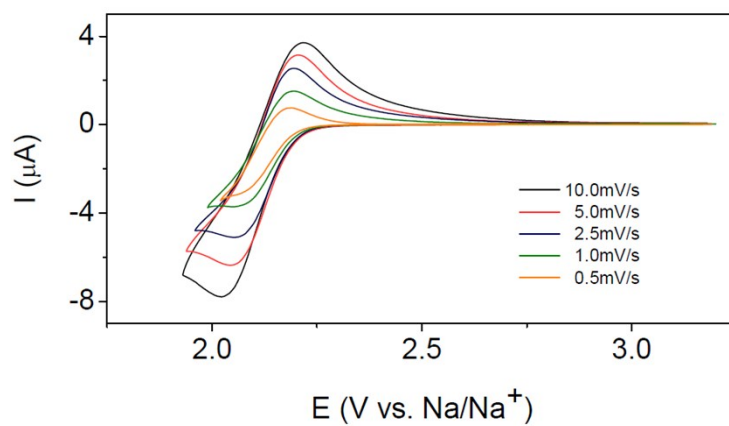
Figure S2. CVs on an Au electrode in O_2 saturated 0.1 M $NaClO_4$ DMSO. Scan rates are from 0.5 to 10 mV/s. The reversibility of the redox of O_2/O_2^- at low scan rates suggests that the O_2^- generated by ORR is highly stable or has long lifetime in the presence of 0.1 M Na^+, and that the reaction rate constant of O_2^- and Na^+ forming solid NaO_2 is small.
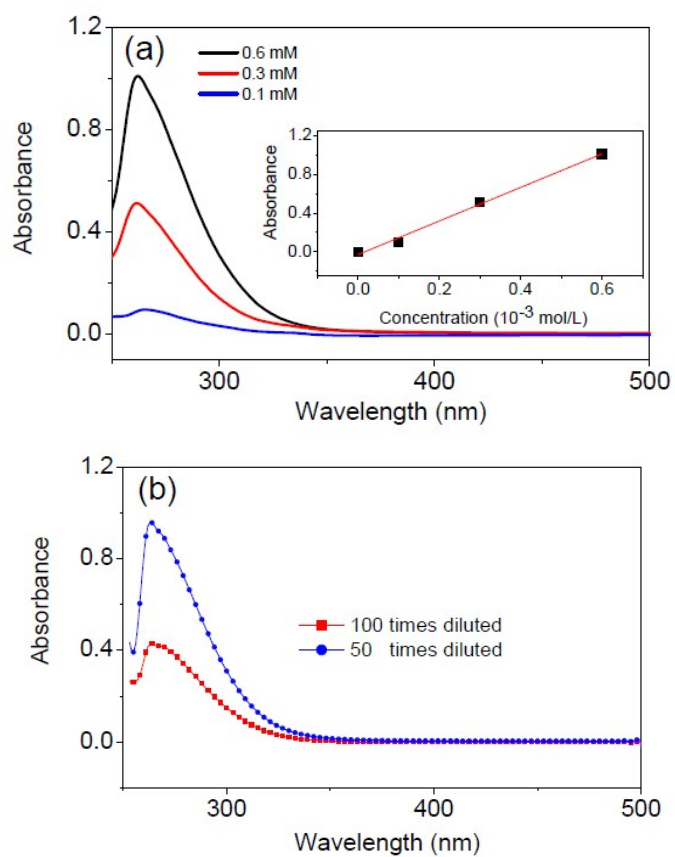
Figure S3. (a) UV-Vis spectra of DMSO containing various concentrations of TMAO$_2$, inset shows the absorbance at 262 nm as a function of [O$_2^-$]. (b) UV-Vis spectra of (red) 50 and (blue) 100 times diluted solutions of NaO$_2$-saturated DMSO.
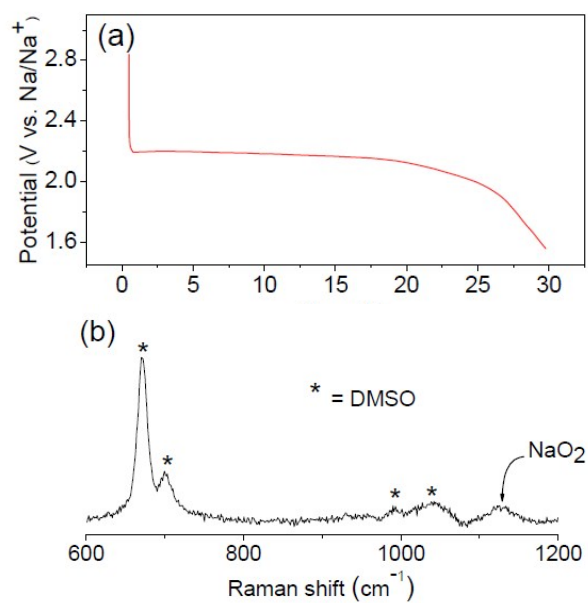
Figure S4. (a) Discharging curve of an Au electrode in an O_2 saturated 0.1 M $NaClO_4$ DMSO at a current density of 318 $\mu A/cm^2$ to the state of "sudden death" with the cathodic cut-off potential of 1.55 V. (b) SERS spectrum collected at the end of discharge showing that the Au surface is dominated with NaO_2.
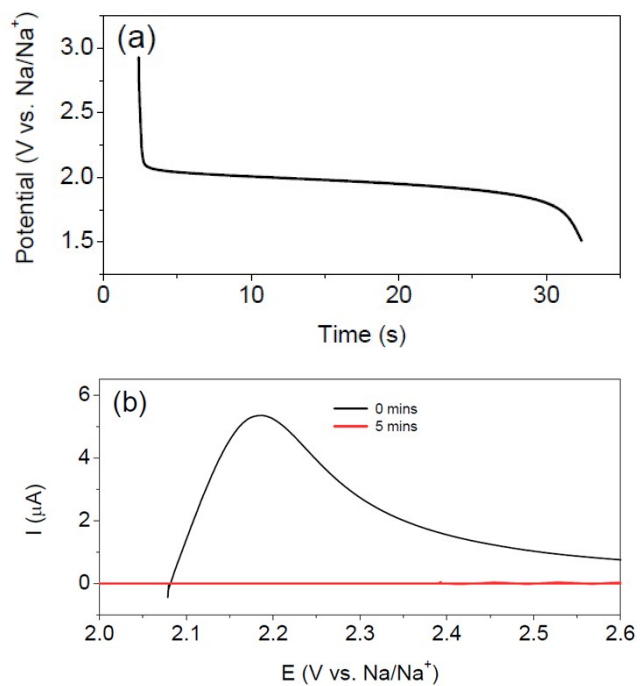
Figure S5. (a) Discharging curve of an Au electrode in O_2 saturated 0.1 M $TBAClO_4$ DMSO at a current density of 318 $\mu A/cm^2$ with the cathodic cut-off potential of 1.55 V. (b) LSV curves of the Au electrode immediately after discharging (black line) and after 5 minutes resting time (red line). Scan rate is 10 mV/s. The disappearance of the oxidation peak after resting indicates that 5 minutes are enough for the free O_2^- to diffuse into bulk electrolyte solution.
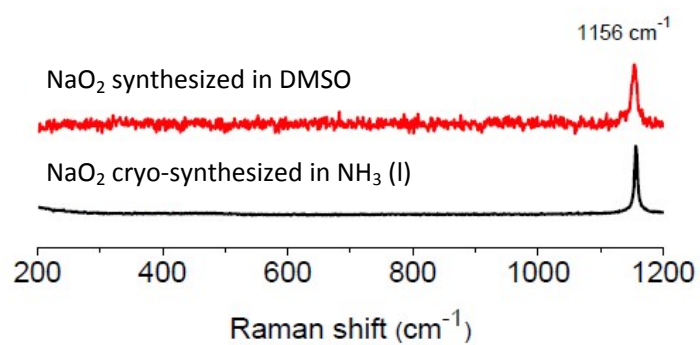
Figure S6. Raman spectra of (black) cryo-synthesized NaO_2 and (red) NaO_2 prepared by reaction of KO_2 and $NaClO_4$ in DMSO. The Raman signature for NaO_2 differs from that observed for NaO_2 on Au by *in situ* SERS by 10 cm^{-1} due to substrate effects.

Table S1 DFT total-energy adsorption energy (ΔE, in eV), O-O stretching frequency (ν_{O-O}, in cm^{-1}), bond length (d_{O-O}, in Å), Bader charge (in electrons), and static surface dipole moment (μ_0, in eÅ) at zero field, of molecular O_2, NaO_2, and Na_2O_2 adsorbed at Au|DMSO interfaces.

	ΔE	ν_{O-O}	d_{O-O}	Charge	μ_0
O_2/Au_1/Au(111)	+0.83	1175	1.300	-0.39	+0.96
NaO_2/Au(211)	-2.00	762	1.450	-0.99	-0.92
Na_2O_2/Au(211)	-3.35	705	1.515	-1.24	-1.32

Results were obtained at the 700 eV cutoff energy level. Adsorption energies were referenced to the respective Au|DMSO interface and each adsorbate as a neutral molecule in the gas phase. See Figure 4 for snapshots of these surface species. The vibrational calculations to determine ν_{O-O} involved relaxing the Na and O_2 group only, and also the Au adatom in the case of O_2/Au_1. The average interfacial electric field (ε) was taken to be 0.3 V/Å; see Ref. S1 for more details about μ_0 and ε.

Table S2. Literature values of the standard-state free energies of formation ($\Delta G°_f$, in eV), and the standard-state free energies of solvation in DMSO ($\Delta G°_{sol}$, in eV).

Species	$\Delta G°_f$ *	$\Delta G°_{sol}$
$Na^+_{(g)}$	+5.95	-4.64 [#]
$O_2^-{}_{(g)}$	-0.45	-2.81 [†]
$NaO_{2(s)}$	-2.27	n/a

*Taken from the NIST-JANAF Thermochemical Tables.

[#]Ref. S2; [†]Ref. S3

Refs. S2 and S3 reported ΔG^*_{sol}, where the standard-state concentration for both gas- and solution-phase Na^+ and O_2^- are taken to be 1 M (i.e., 1 mol per liter of space or solution). These values have been converted to $\Delta G°_{sol}$, where the standard-state concentrations for the gas- and solution-phase ions are 1 mol at 1 atm, and 1 M, respectively, by adding 0.082 eV.

References

S1 S. H. Rawal, W. C. McKee and Y. Xu, to be submitted.

S2 C. P. Kelly, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B,* 2007, **111**, 408-422.

S3 D. G. Kwabi, V. S. Bryantsev, T. P. Batcho, D. M. Itkis, C. V. Thompson and Y. Shao-Horn, *Angew. Chem.* 2016, **128**, 3181-3186.