Supporting information

In Situ Detection of Reactive Oxygen Species Spontaneously Generated on Lead Acid Battery Anodes: A Pathway for Degradation and Self-Discharge at Open Circuit

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1- *Ex-situ* characterization of fresh Pb-C anode

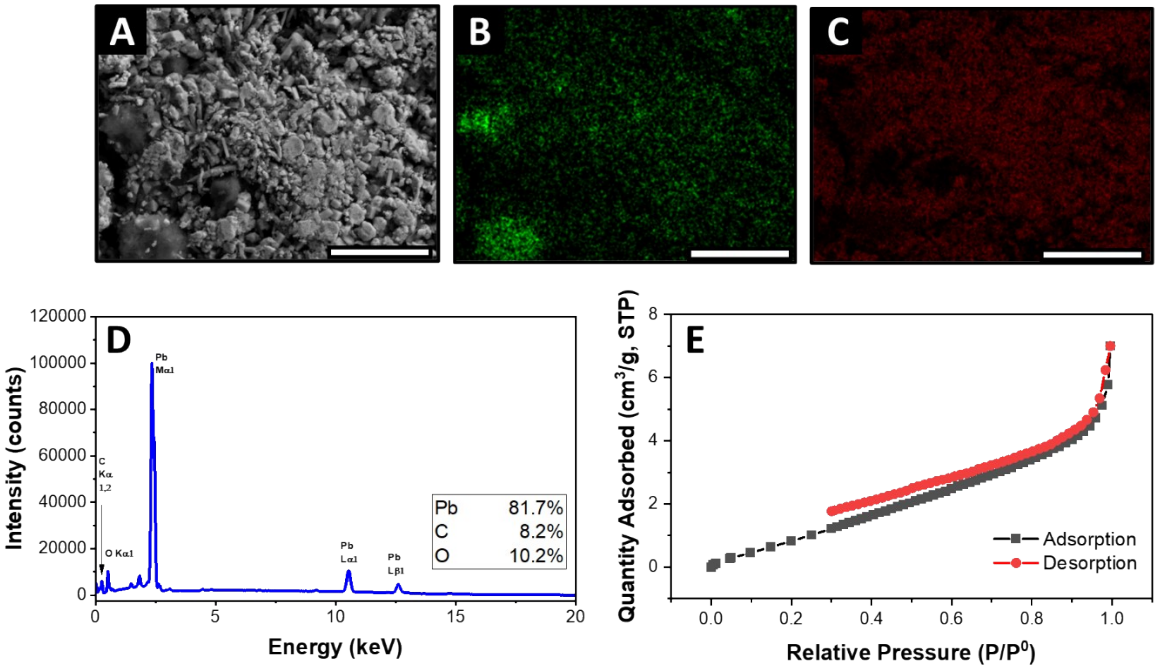

Figure S1: Characterization of Pb anodes. (A) SEM image of commercial Pb anodes. (B) Corresponding EDX mapping of carbon. (C) EDX mapping of Pb. (D) EDX spectrum of the region showing Pb, C, and O only. (E) BET adsorption isotherm. The BET surface area was calculated to be 5.95 m^2/g, highlighting the roughness of the Pb surface.

2- ESR Signatures of Radical Adducts with DMPO as a trapping molecule.

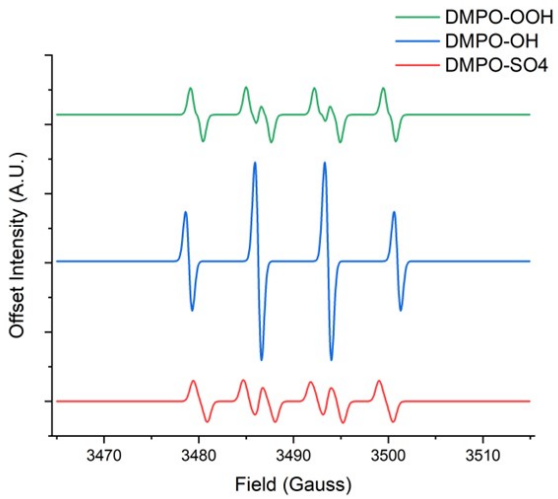

Figure S2: Distinct ESR signatures of the radical adducts formed when different radical species ($OOH^{\cdot}$, $OH^{\cdot}$, $SO_4^{\cdot}$) are trapped by DMPO.

3- Galvanostatic cycling and *ex-situ* characterization of Pb-C anode and pure Pb strip

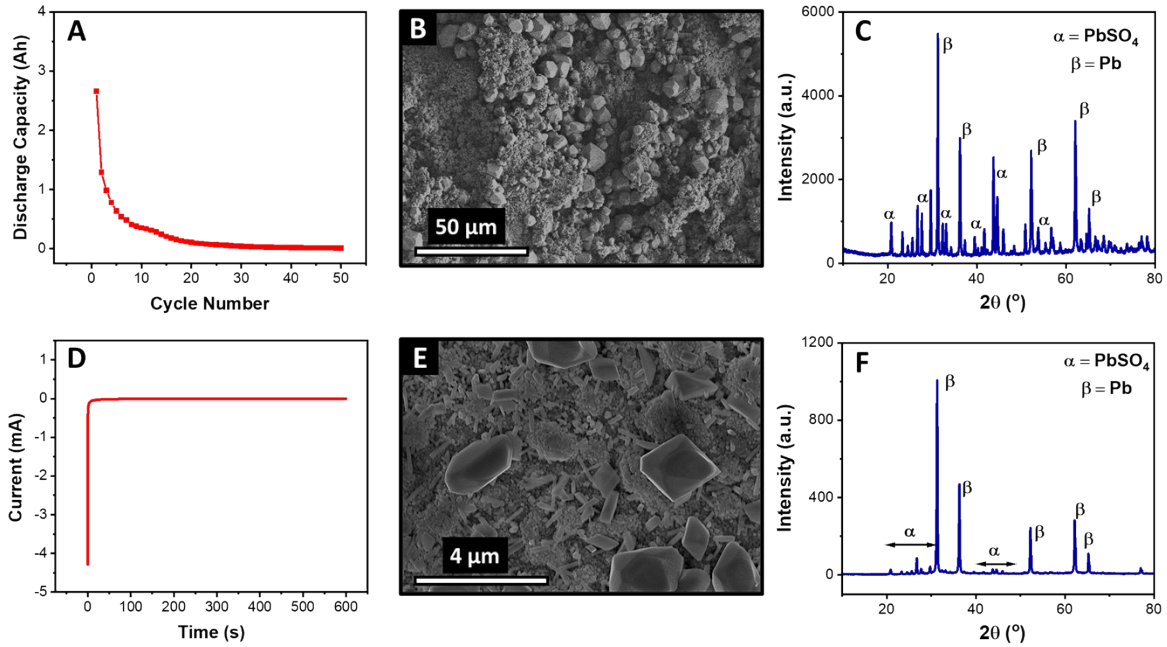

Figure S3: Sulfation conditions for Pb surfaces and the $PbSO_4$ crystals. (A) Discharging of commercial LAB anode in 4.2 M H_2SO_4 electrolyte. (B) $PbSO_4$ crystals formed on discharge (C) XRD showing the development of peaks of $PbSO_4$ after discharge (D) Anodic polarization of Pb strip in 4.2 M H_2SO_4 at 0.1 V v/s Ag/AgCl/ 3 M KCl for 600 s (E) $PbSO_4$ crystals formed during anodic polarization (F) XRD showing the development of peaks of $PbSO_4$ after polarization..

4- *Ex-situ* characterization of self-sulfated pure Pb strips

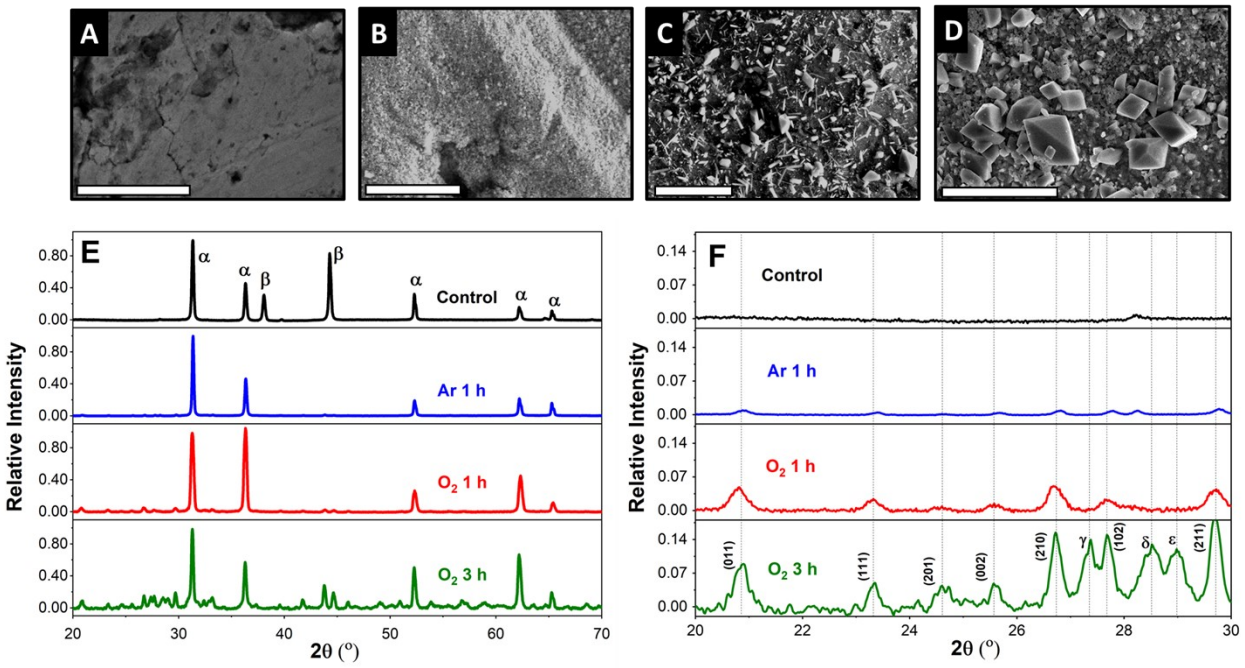

Figure S4: SEM images and X-ray diffractograms of Pb strips. SEM images of (A) clean Pb strips (B) Pb strip immersed in Ar-saturated 4.2 M H_2SO_4 for 1 h, (C) Pb strip immersed in O_2-saturated 4.2 M H_2SO_4 for 1 h, (D) Pb strip immersed in O_2-saturated 4.2 M H_2SO_4 for 3 h. Scale bars are 5 µm each. X-ray diffractograms showing (E) growth of $PbSO_4$ and Pb oxide peaks with immersion of Pb sheets in 4.2 M H_2SO_4 in the presence of Ar and O_2, (F) comparison of peak intensities of $PbSO_4$ (110) across the immersed Pb strips. The peaks are denoted as follows: α = Pb β = Al from the XRD holder, γ = Pb_3O_4, δ = α-type PbO_2, ε = fluorite-type PbO_2. Peaks denoted by planes belong to $PbSO_4$.

In the SEM of a fresh Pb strip before immersing it in 4.2 M H_2SO_4 (Figure S4A), we observe a clean and flat surface. When immersed in 4.2 M H_2SO_4 saturated with Ar, the flatness of the surface is largely retained (Figure S4B). We observed some tiny crystals have formed on the Pb surface which could belong to $PbSO_4$. The corresponding XRD shows some peaks developing in the spectrum that belong to $PbSO_4$ (Figure S4E and F, blue curves), confirming that HER is indeed happening on the Pb strip, forming $PbSO_4$. The relative intensity of the (011) peak is about 0.01, showing that only minute amounts of $PbSO_4$ are formed in the absence of O_2. This is expected, considering that the Pb strips are flat and smooth, and having much less area compared to Pb anodes, leading to less intense HER. In contrast, when the Pb strip is immersed in 4.2 M H_2SO_4 saturated with O_2 for 1 h, larger crystals of ~1 µm size are observed in the SEM (Figure S4C).

These crystals grow even further (2-3 µm) when the immersion time is increased to 3 h (Figure S3D) and start to resemble the polygonal crystals typical of $PbSO_4$ formed on LAB anodes during the discharge process (Figure S4E). Moreover, in the corresponding XRD spectra, the relative intensity of the $PbSO_4$ (110) peak grows to 0.05 after 1 h (Figure S3E and F, red curve) and 0.09 after 3 h (Figure S4E and F, green curve). Hence, we can confirm that Pb strips are rapidly sulfated when immersed in H_2SO_4 in the presence of O_2. The observations from the Pb strips are similar to those in the Pb anodes, indicating that carbon additives have a minimal impact. Furthermore, we can also conclude that reactions involving O_2 contribute to sulfation much more than HER on Pb surfaces.

5- Calibration curve of H_2O_2 sensor (Pt UME)

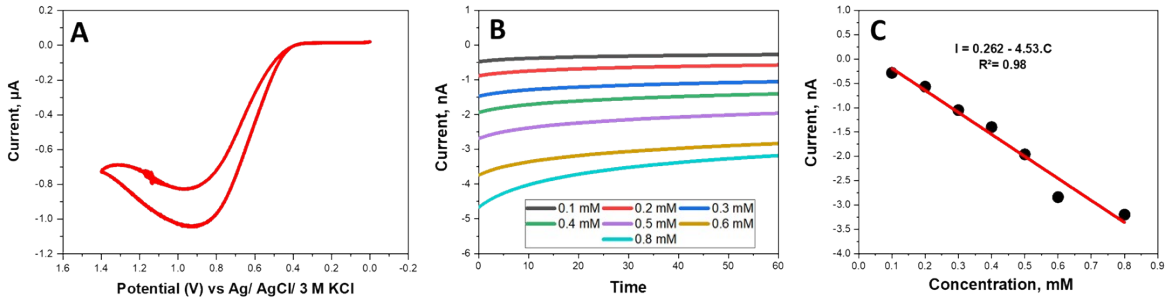

Figure S5: Calibration of transient tip current measured at the Pt UME SECM probe versus known H_2O_2 concentration. (A) Cyclic voltammogram (CV) showing the redox peak corresponding to oxidation of H_2O_2 at ~0.9 V vs Ag/AgCl/ 3 M KCl (B) Chronoamperometric (current vs time) curves at different known H_2O_2 concentrations. (C) Linear calibration curve of current at 60 s vs H_2O_2 concentration.

6- ESR of pure Pb strips in Ar and O_2 conditions

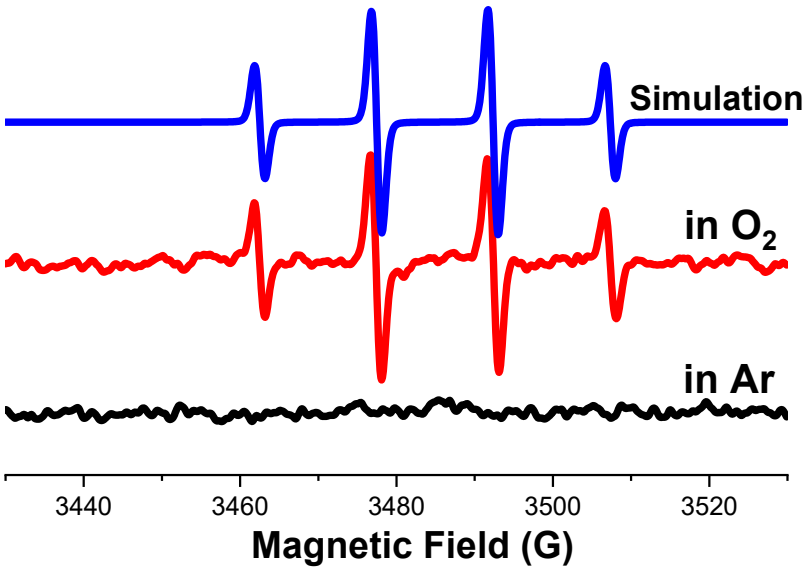

Figure S6: Detection of $OH^{\bullet}$ on Pb strip soaked in 0.5 M H_2SO_4 + 100 mM DMPO for 1 hour. Under deaerated (purging Ar) conditions, no paramagnetic signals are observed (black curve). Under aerated (purging O_2) conditions, the splitting feature (1:2:2:1 integration ratio) for the $[DMPO{-}OH]^{\bullet}$ radical adduct is observed (red curve) which fits well with the Easy Spin simulated data (blue curve).

7- Control experiments for *in-situ* detection of OH• radicals

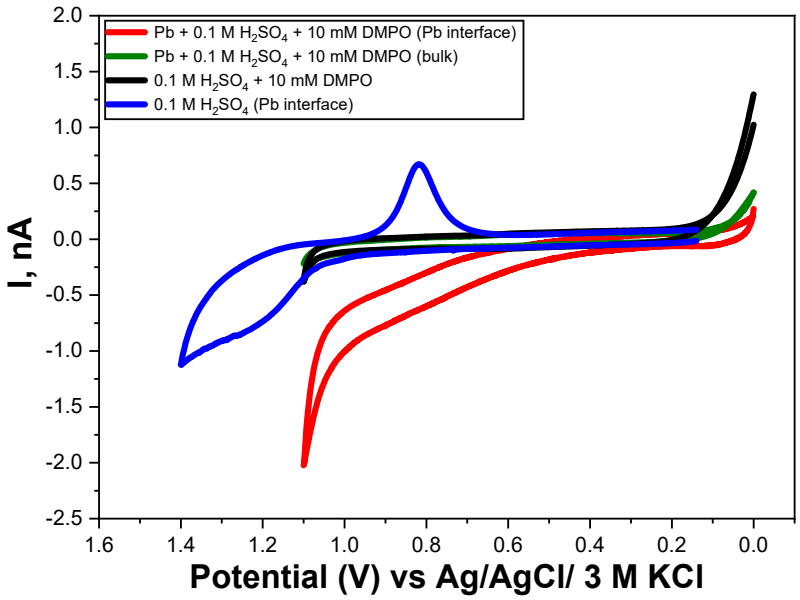

Figure S7: Control experiments for the detection of [DMPO−OH]• at the Au-UME probe.

We performed the first additional control experiments by positioning the Au-UME at the close vicinity of the commercial Pb anode (d = 10 µm) and using 0.5 M H_2SO_4 without DMPO as the testing electrolyte. The recorded cyclic voltammogram (CV) at the Au-UME is shown in Figure S7 (blue curve). As can be seen, the CV exactly matches the behavior of Au in H_2SO_4 revealing an oxidation peak at about 1 V vs Ag/AgCl/ 3 M KCl corresponding to the formation of surface Au oxides. The reduction peak observed at about 0.8 V is assigned to the reduction of these Au oxides. In the second control experiment, we recorded the CV between 0.1 and 1.1 V in a solution 0.5 M H_2SO_4 + 10 mM DMPO without immersing the commercial Pb anode in it. Interestingly, no significant current was measured between 0.1 V and 1.1 V vs Ag/AgCl/ 3 M KCl in both cases, which implies that the oxidation wave measured in the presence of DMPO is due to the oxidation of DMPO-OH at the Au-UME.