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Selective electroreduction of CO_2 to formate on 3D [100] Pb dendrites with nanometer-sized needle-like tips

Supplementary Information

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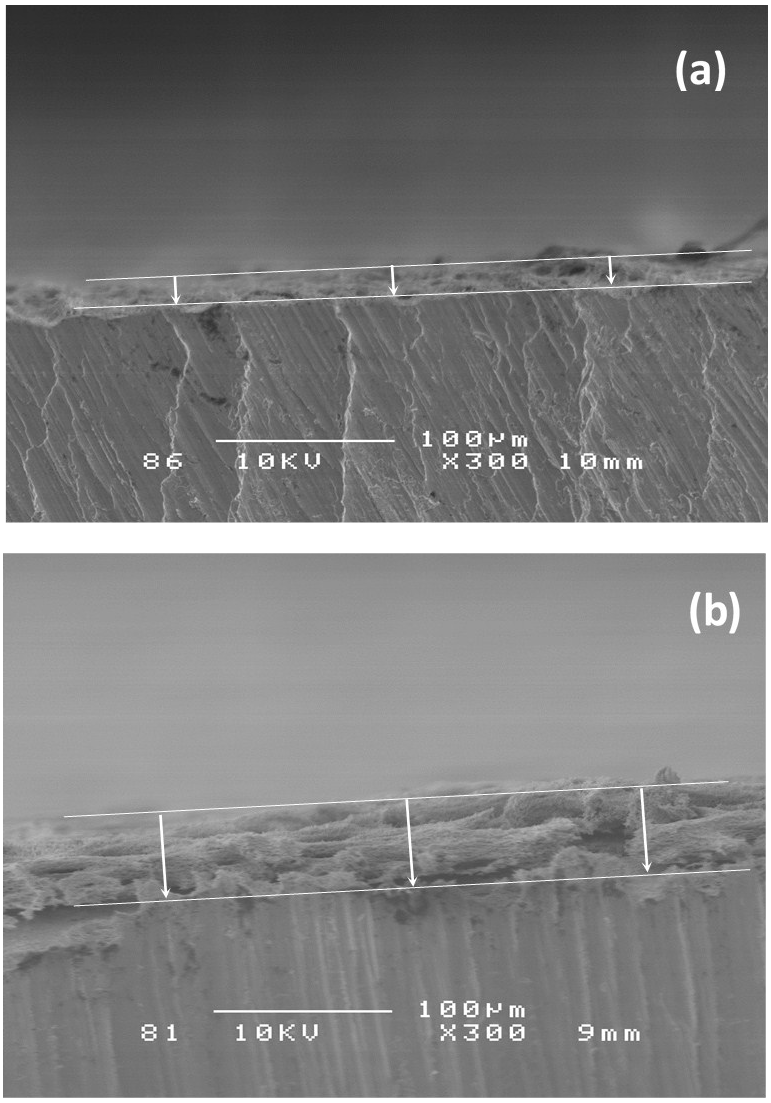

Figure S1. SEM cross-sections of porous Pb film on Pb plate, deposited at (a) -1 A cm^{-2}, and (b) -4 A cm^{-2}. The deposition time was 20 seconds.

The thicknesses of porous Pb films were measured by SEM cross-section. When deposition time is fixed, the thickness of porous Pb film increased with deposition current density. Figure S1(a) shows the thickness of porous Pb film deposited at -1 A cm^{-2} is ~20 μm. When current density increased to -4 A cm^{-2}, the thickness of porous Pb film increased to 48 μm (Figure S1(b)).

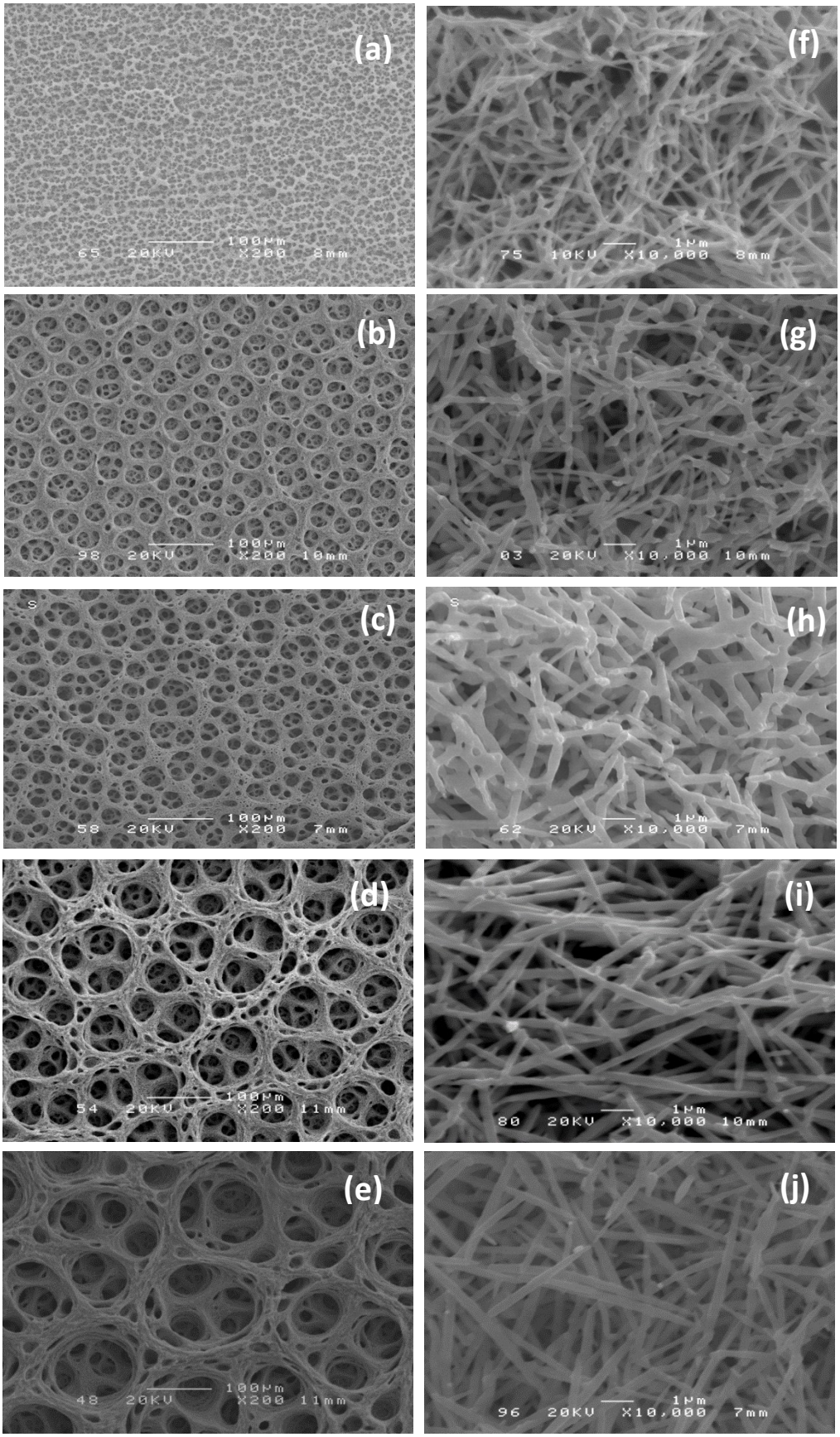

Figure S2. SEM images of porous Pb films deposited at (a, f) 3 seconds, (b, g) 10 seconds, (c, h) 20 seconds, (d, i) 40 seconds and (e, j) 60 seconds. The deposition current density was -4 A cm^{-2}.

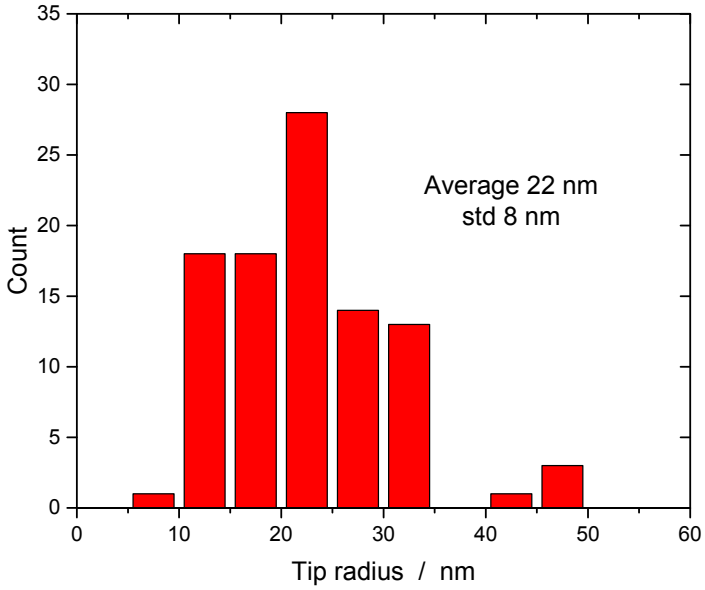

Figure S3. Histogram of the tip radius. The tip radius of a total of 96 dendrites were measured from SEM micrographs of samples prepared at different deposition current densities and deposition times.

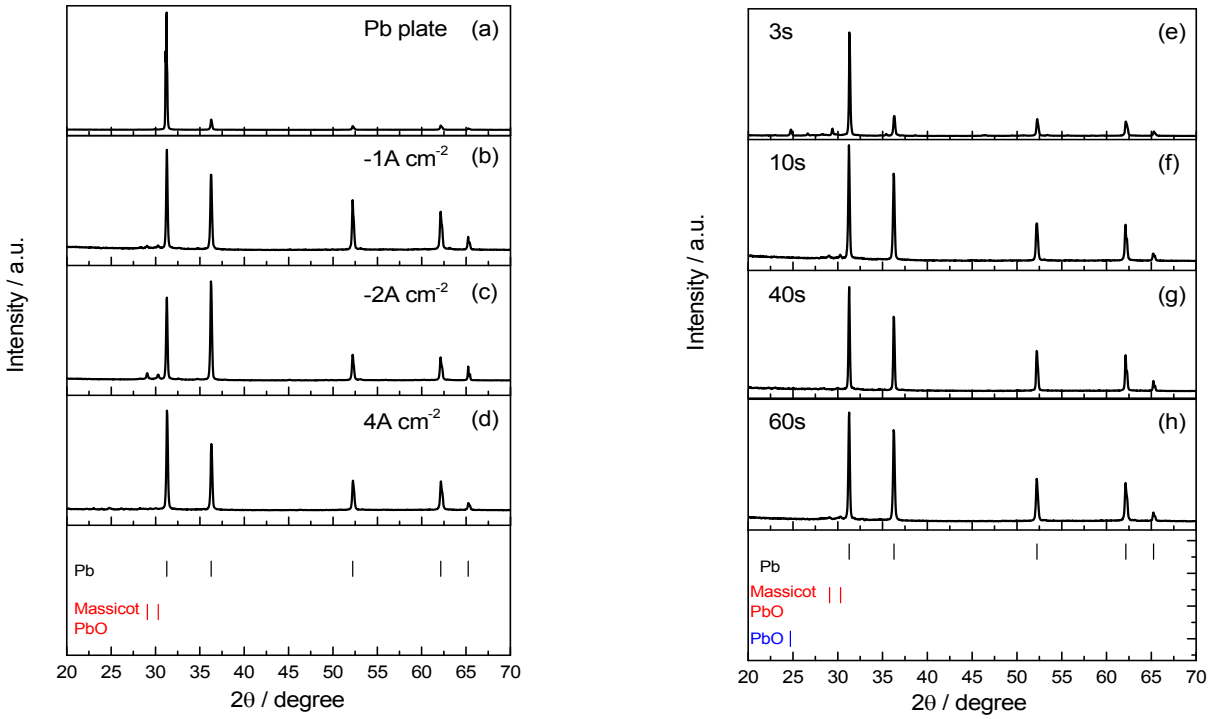

Figure S4. XRD patterns of (a) Pb plate; and porous Pb films deposited at (b) -1 A cm^{-2}; (c) -2 A cm^{-2}; (d) -4 A cm^{-2}; for a deposition time of 20 seconds. XRD patterns of porous Pb films deposited at (e) 3 seconds; (f) 10 seconds; (g) 40 seconds; and (h) 60 seconds. The deposition current density was -4 A cm^{-2}.

The XRD patterns indicate that all samples shown in Figures 1 and 2 are primarily composed of metallic Pb, with the characteristic XRD peaks at 31.2° (111); 36.2° (200); 52.2° (220); 62.1° (311), 65.2° (222). Very small peaks are also observed few surfaces were oxidized at 24.7° (PbO), and 29.1° and 30.3° (massicot PbO). On the Pb plate, the intensity of the (111) plane at 31.2° is very strong indicating the substrate is preferentially oriented along that axis.

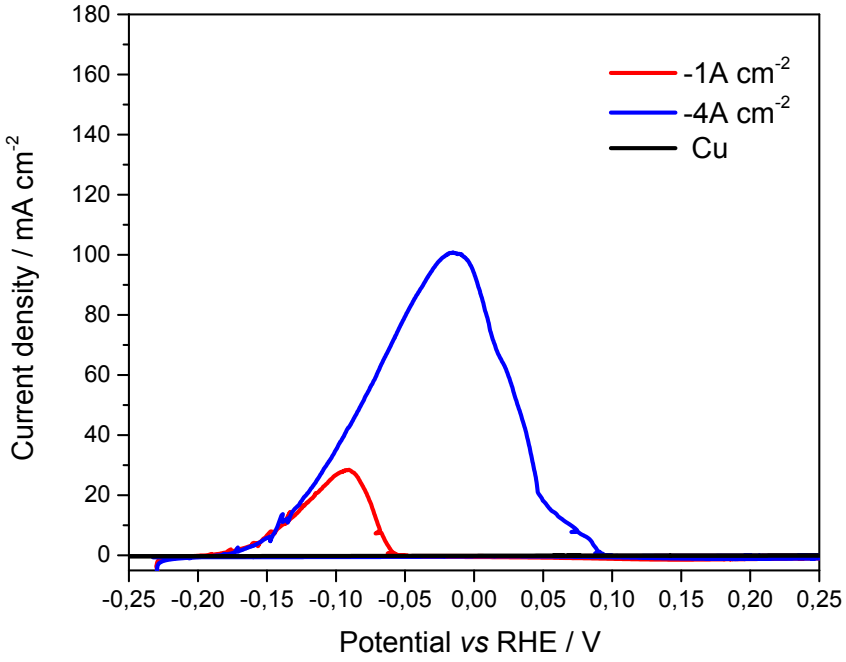

Figure S5. Stripping voltammograms of porous Pb/Cu films at 5 mV s^{-1} in 1 M $HClO_4$.

To quantify the mass of lead in the porous Pb films, Pb was first deposited on 0.5 cm^2 Cu plate at the same conditions as Pb depositing on Pb plate. After deposition, stripping voltammetry was carried out in 1 M $HClO_4$ at 5 mV s^{-1}. Pb films have obvious stripping peaks and the peak integration area increases with deposition current density. However, the Cu substrate did not show a stripping peak in the range of -0.25 V to 0.25 V. The mass of deposited film may be calculated as $Q*M/nF$, in which Q is the charge for reducing Pb film per cm^2; M is the molar mass of Pb (207.2 g mol^{-1}); n is the electron transfer number (n=2), and F is the Faradaic constant (96485 C mol^{-1}). The Cu substrate does not show any stripping peak in the range of -0.25 V to 0.25 V. In

comparison, porous Pb films have obvious stripping peaks and the peak integration area increases with deposition current density.

The Pb deposition charge efficiency may be calculated by determining the ratio of the Pb stripping charge to the total cathodic charge (Pb^{+2} reduction and H_2 evolution) during the deposition. The charge efficiency of Pb deposition under varying conditions is similar (~2.5%) and does not vary significantly with the deposition current density and deposition times.

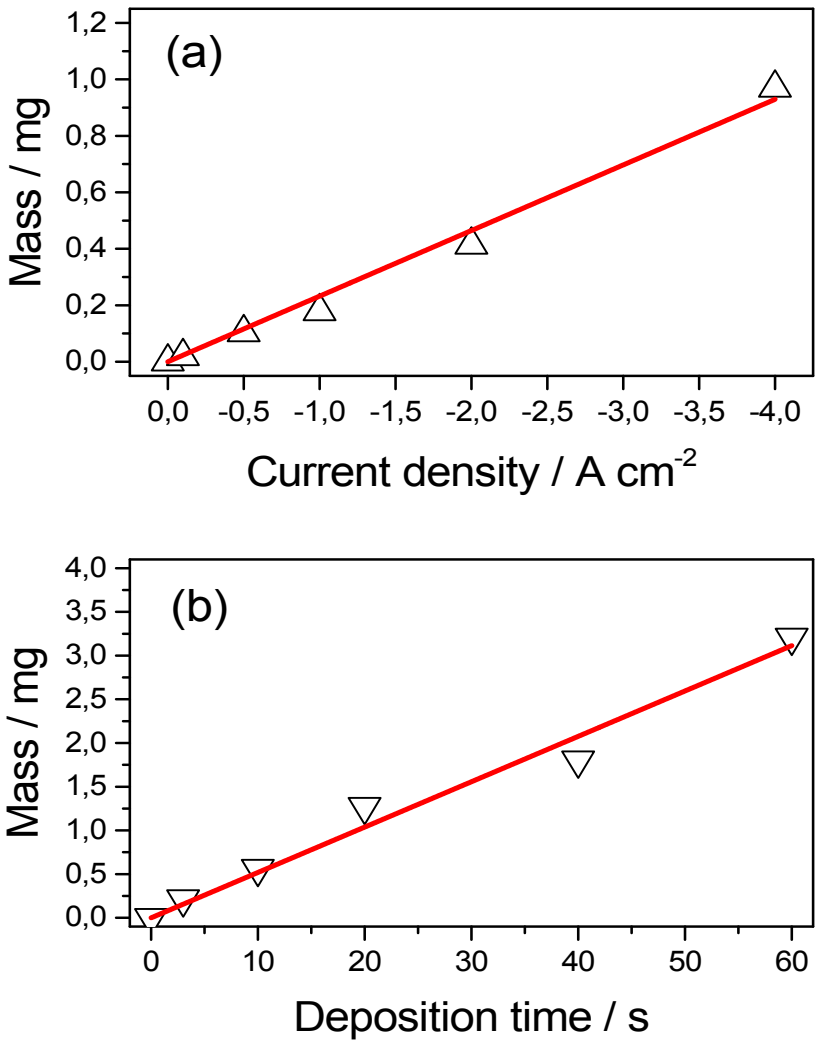

Figure S6. Variation of mass for porous Pb films with respect to (a) deposition current density and (b) deposition time.

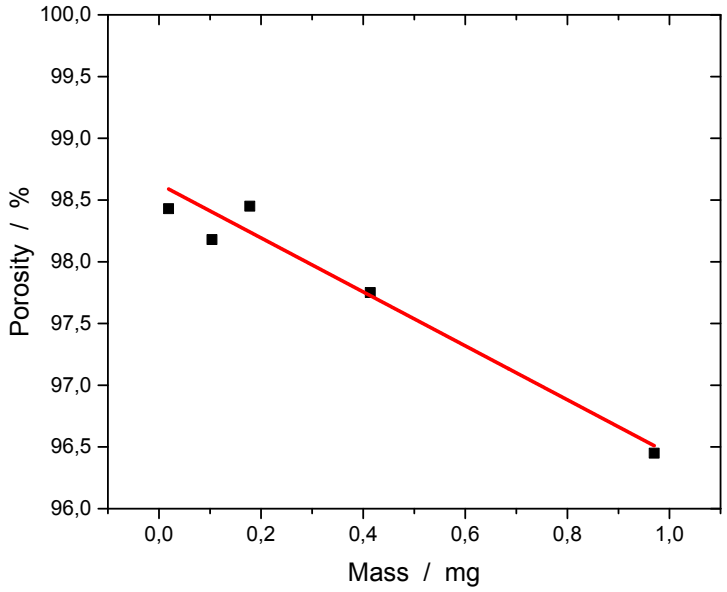

Figure S7. Variation of porosity with respect to the mass of lead. The deposition time was fixed at 20s and the deposition current density was increased from 0.1 to 4.0 mA cm^{-2}.

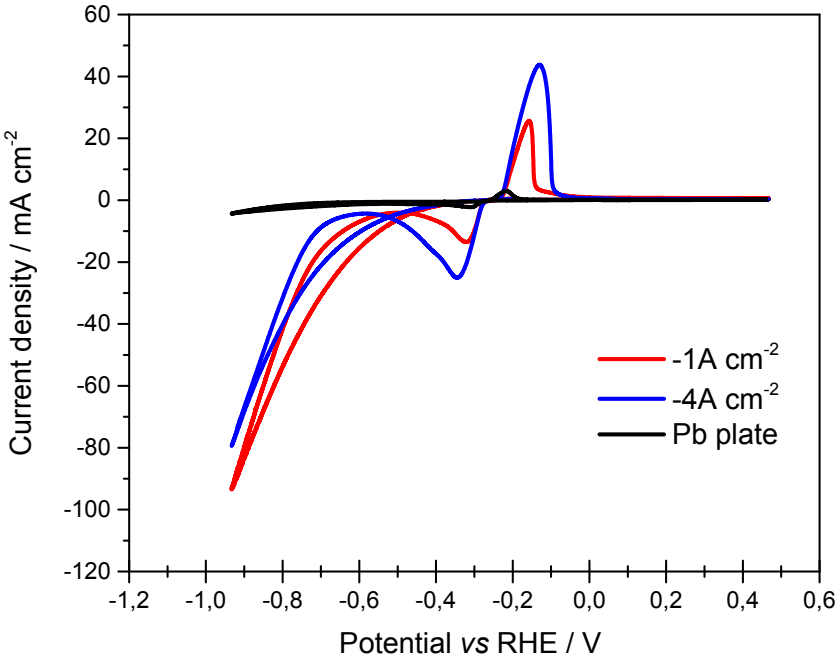

Figure S8. CVs in 0.5 M H_2SO_4 solution at 5 mV s^{-1}.

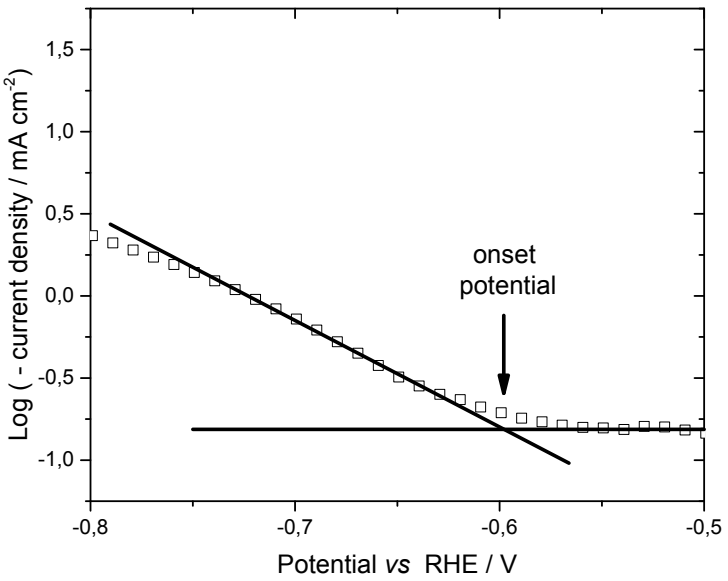

Figure S9. Variation of log (-j) with respect to the electrode potential in linear sweep voltammogram of porous Pb films in CO_2-saturated 1M $KHCO_3$. The scan rate was 5 mV s^{-1}. The porous Pb film was deposited at -4 A cm^{-2} and 40 seconds.

The onset potential for H_2 evolution and CO_2 electroreduction was assessed by drawing log(*-j*) *vs* potential curves like the one shown in Figure S9 and taking the onset potential as the potential at which the solid lines intersect each other.

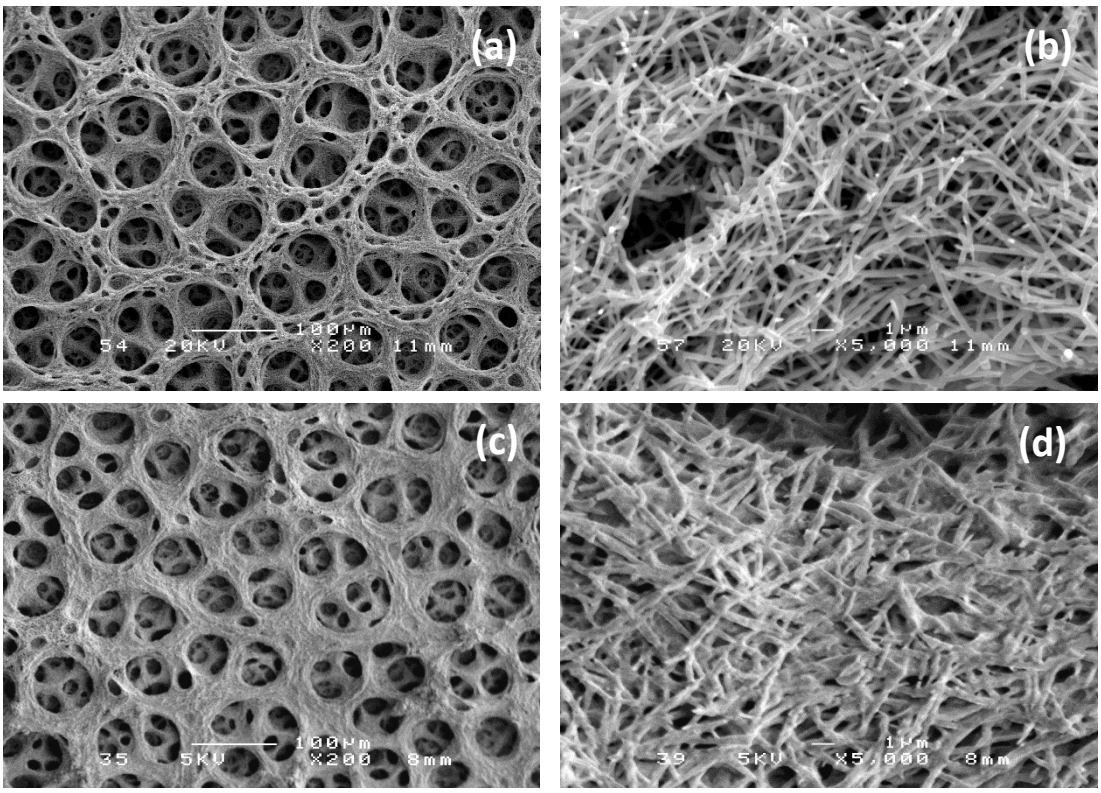

Figure S10. SEM images of porous Pb films (a-b) before; and (c-d) after 100 minutes of CO_2 electrolysis.

The morphology of porous Pb electrode is quite stable. Even after 100 minutes of electrolysis, there were no obvious differences in the porous structure and needle-like secondary structure. However, the porous film appears denser as some interspaces between the needles structures were occupied by carbonate salt originating from the electrolyte.

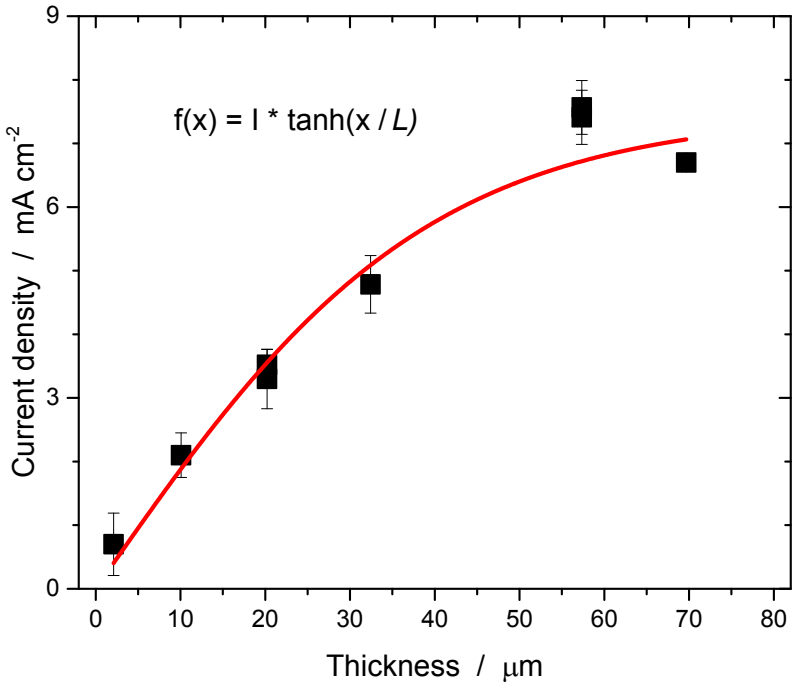

Figure S11. Variation of the current density with respect to the thickness of the deposit. The curve shows the best fit obtained using a function f(x) = I * tanh(x / L).

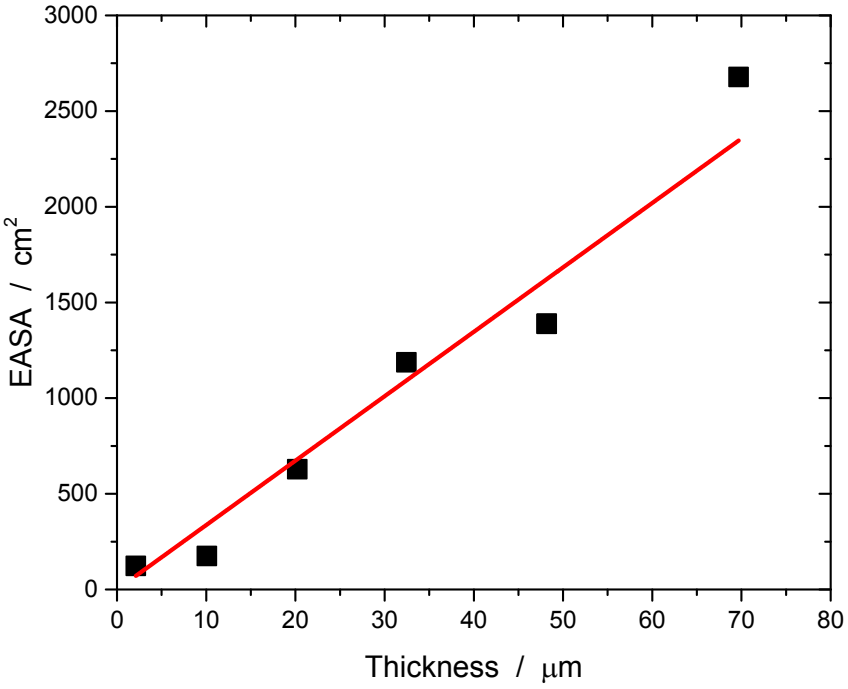

Figure S12. Variation of EASA with respect to the thickness of the deposit.

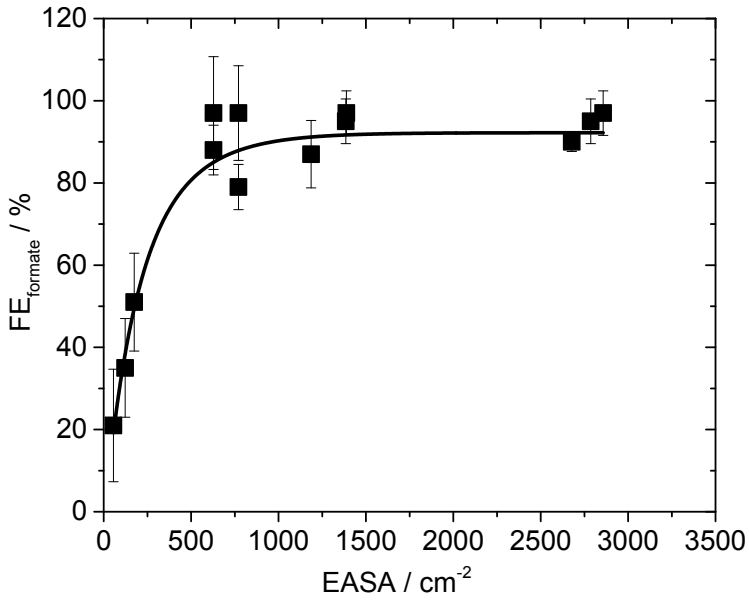

Figure S13. Variation of formate Faradic Efficiency with respect to the Electrochemically Active Surface Area. The EASA of all porous Pb films prepared in the present study are shown.

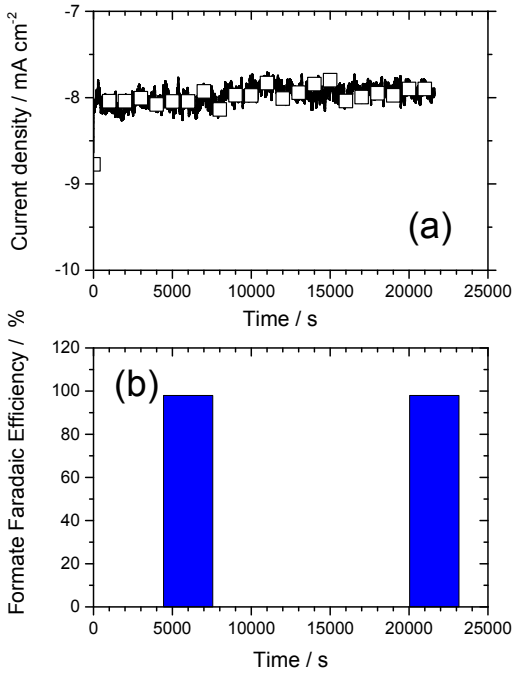

Figure S14. Variation of (a) the current density and (b) the formate faradaic efficiency as a function of the polarization time. These measurements were performed on $Pb_{4\text{-}40}$ at -0.99 V in CO_2-saturated 1M $KHCO_3$.

Table S1. Integration area of $Pb \leftrightarrow Pb^{2+}$ redox peaks

Samples		Integration charge of oxide peak (C) $Pb \rightarrow Pb^{2+}$	Integration charge of reduction peak (C) $Pb^{2+} \rightarrow Pb$	Charge percentage of oxide peak and reduction peak (%)
-4A cm^{-2}	3 s	0.216	0.210	51:49
	10 s	0.389	0.404	49:51
	20 s	0.388	0.428	48:52
	40 s	0.780	0.792	50:50
	60 s	0.750	0.746	50:50
20 s	-1 A cm^{-2}	0.176	0.174	50:50
	-2 A cm^{-2}	0.332	0.361	48:52
	-4 A cm^{-2}	0.387	0.386	50:50
	-4 A cm^{-2}	0.397	0.396	50:50