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Supporting Information

CO_2 electrolysis in seawater: calcification effect and a hybrid self-powered concept

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Experimental Section

Materials and Chemicals: Magnesium alloy (AZ31) rods with the nominal mass composition 96% Mg, 3% Al, and 1% Zn were purchased from Goodfellow Metals, UK. Silver foils (0.125 mm, 99.99 %, Advent Research Materials) were used as substrates for formation of Ag/AgCl. Prior to use, silver foils were cleaned via ultrasonication in acetone, ethanol, followed by rinsing with Milli-Q water (18 MΩ·cm) and drying the samples in a nitrogen stream. Similar procedure was employed for magnesium alloy rods except they were firstly polished to obtain shinny surface by using fine sandpapers. The chemicals (NaCl, $MgCl_2$, Na_2SO_4, KCl, $CaCl_2$, ethanol, acetone) were purchased from ChemSupply, and used as-received. Milli-Q water was used in all aqueous-based experiments. The seawater sample was collected from the North Wollongong beach, Australia, and used without further treatment.

Electrochemical experiment and anodization: All electrochemical experiments were performed with a CH Instrument 650D or a Biologic VSP potentiostat at 20 ± 2 °C. For anodisation, a three-electrode configuration was employed with a Ag foil as the anode, a platinum foil as a counter electrode, and an Ag/AgCl (3M NaCl) as a reference electrode. After anodisation at 1.0 V in 0.6 M NaCl solution, the Ag/AgCl samples were rinsed with Milli-Q water and then dried in a nitrogen stream.

CO_2 electroreduction: Prior to use, both seawater and 3.5 wt % NaCl electrolytes were purged with CO_2 for several hours; as expected due to acidification, the pH of the electrolyte dropped (eg. seawater from ~ 8.0 to ~ 4.8, whilst 3.5 wt % NaCl from ~ 6.5 to ~ 4.0). A two-compartment gastight glass H-cell with a three-electrode configuration was used for electrochemical CO_2 reduction. The cathodic and anodic compartments were either separated by a Nafion membrane (Nafion® 117, FuelCellsEtc.) or a glass frit. All the potentials were

measured and reported against the reference electrode (Ag/AgCl 3M NaCl). For a three-electrode half-cell study, prior to the CO_2 reduction, the as anodised Ag/AgCl working electrode was reduced to nanoporous Ag at a constant potential of -1.4 V in 3.5 wt % NaCl for 15 min with a constant CO_2 (99.99%, BOC) flow at 20 mL min^{-1}. The cell was purging with CO_2 for 15 min, before the CO_2 reduction was carried out at different potentials in either 3.5 wt % NaCl or seawater electrolytes. The electrolyte was magnetically stirred at 250 rpm to enhance the mass transport of CO_2. All the constant potential experiments were corrected using the automatic iR compensation function on the potentiostat, unless otherwise stated. The current density reported in this work was normalised to the geometric surface area. The voltammetry experiments were performed as the above configurations, but without iR correction. During the electrolysis, CO_2 was continuously bubbled into the cathodic compartment at a rate of 20.0 mL min^{-1} controlled by a mass flow controller (GFC17, Aalborg®) and vented directly into the gas-sampling loop (1 mL) of a gas chromatograph (GC) (8610C, SRI Instruments). The average of the results from three measurements was used in the data analysis. Long term stability experiment was DAIgo performed at extended hours with the analysis at the designated interval times. The GC was equipped with a packed MolSieve 5A column and a packed Haysep D column. Argon was used as the carrier gas. A fame ionization detector (FID) with methanizer was used to quantify CO, and a thermal conductivity detector (TCD) was used to quantify H_2. An external standard method was adopted with a standard gas mixture (BOC) composed of H_2, CO, CH_4, C_2H_4, C_2H_6 and CO_2. Liquid products were analysed by using a 400 MHz NMR spectrometer (Bruker Avance) at 30ºC and quantified based on previously reported method.[1,2]

Variations in the pHs of unbuffered NaCl and seawater electrolytes (eg. final pH of ~ 6 to ~ 6.5 after 1 h electrolysis) occurred during the controlled potential electrolysis at different potentials, therefore Tafel analysis was not attempted. In the examination of the impact of cations and anions presence in the seawater towards CO_2 reduction performance, $MgCl_2$, Na_2SO_4, KCl and $CaCl_2$ with desirable molarity were achieved by injection of aliquots of concentrated solutions to the cathodic compartment of the cell containing 3.5 wt % NaCl electrolyte. In the self-powered two-compartment full-cell assembly, a Mg alloy anode was wired to a Ag/AgCl or a Ag foil cathode; and H_2 and CO gases were collected through ≈ 40 μL aliquots of headspace gas removed from their respective compartment using a gas-tight syringe (SGE). The measurements were performed in triplicated, reported in a standard calculation of mean ± standard deviation. The employed 3.5 wt % NaCl and seawater electrolytes were pre-purged and saturated with CO_2 prior to the experiment and also within the assembly. Open circuit potential (OCP) and chronopotentiometry measurements were performed by a potentiostat.

Structural characterization: The Ag- and Mg-based samples were analyzed by X-ray diffraction (XRD, GBC MMA diffractometer) with Cu Kα radiation at a scan rate of 2 degree per min. The morphologies of the samples were investigated by a field emission scanning electron microscopy (FESEM, JEOL JSM-7500FA). X-ray photoelectron spectroscopy (XPS) was measured on a SPECS PHOIBOS 100 Analyser with X-ray excitation provided by Al Kα radiation (hv = 1486.6 eV) at a voltage of 12 kV and a power of 120 W. The XPS binding energy spectra were recorded at a pass-energy of 20 eV in the fixed analyser transmission mode. All the spectra were calibrated by C 1s = 284.6 eV. Raman Spectra were recorded on a Jobin Yvon Horiba HR800 Raman microscope using a 632 nm laser line.

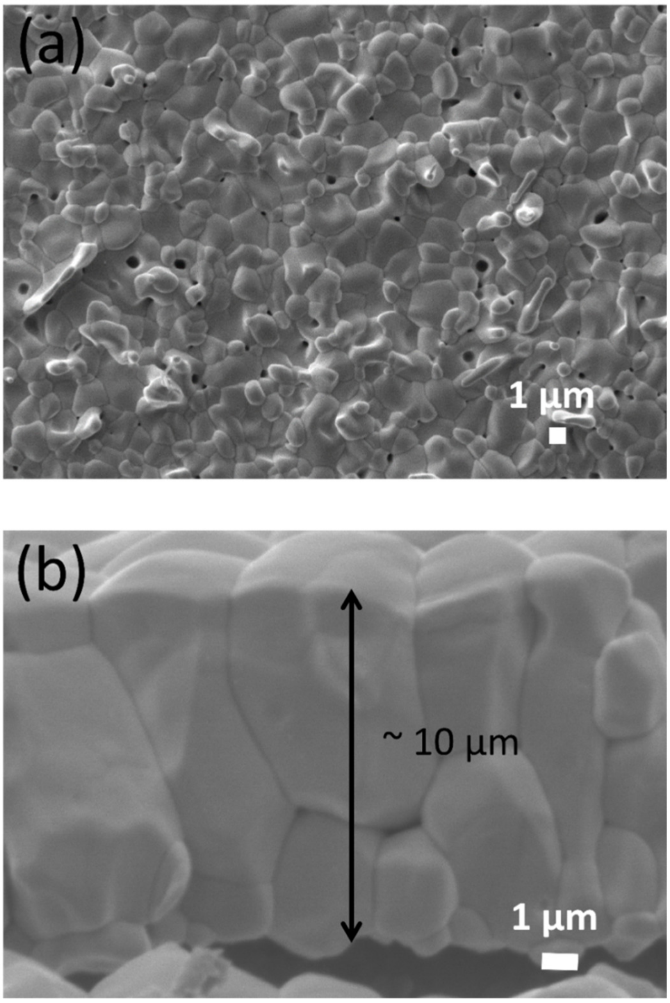

Figure S1 Top view (a) and cross-sectional (b) SEM images of the as prepared Ag/AgCl film after anodization of a Ag foil in 0.6 M NaCl at 1.0 V for 300 s.

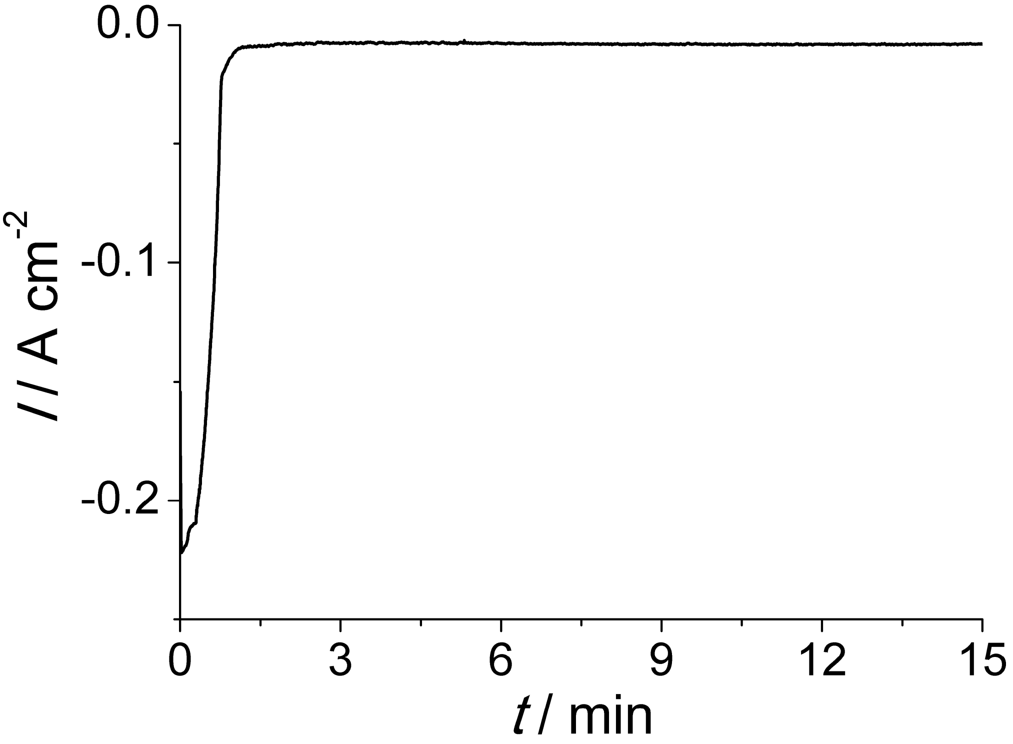

Figure S2 Current-time profile of the electroreduction of Ag/AgCl to form Ag/nanoporous Ag in 3.5 wt % NaCl, at -1.4 V (vs. Ag/AgCl (3M NaCl)).

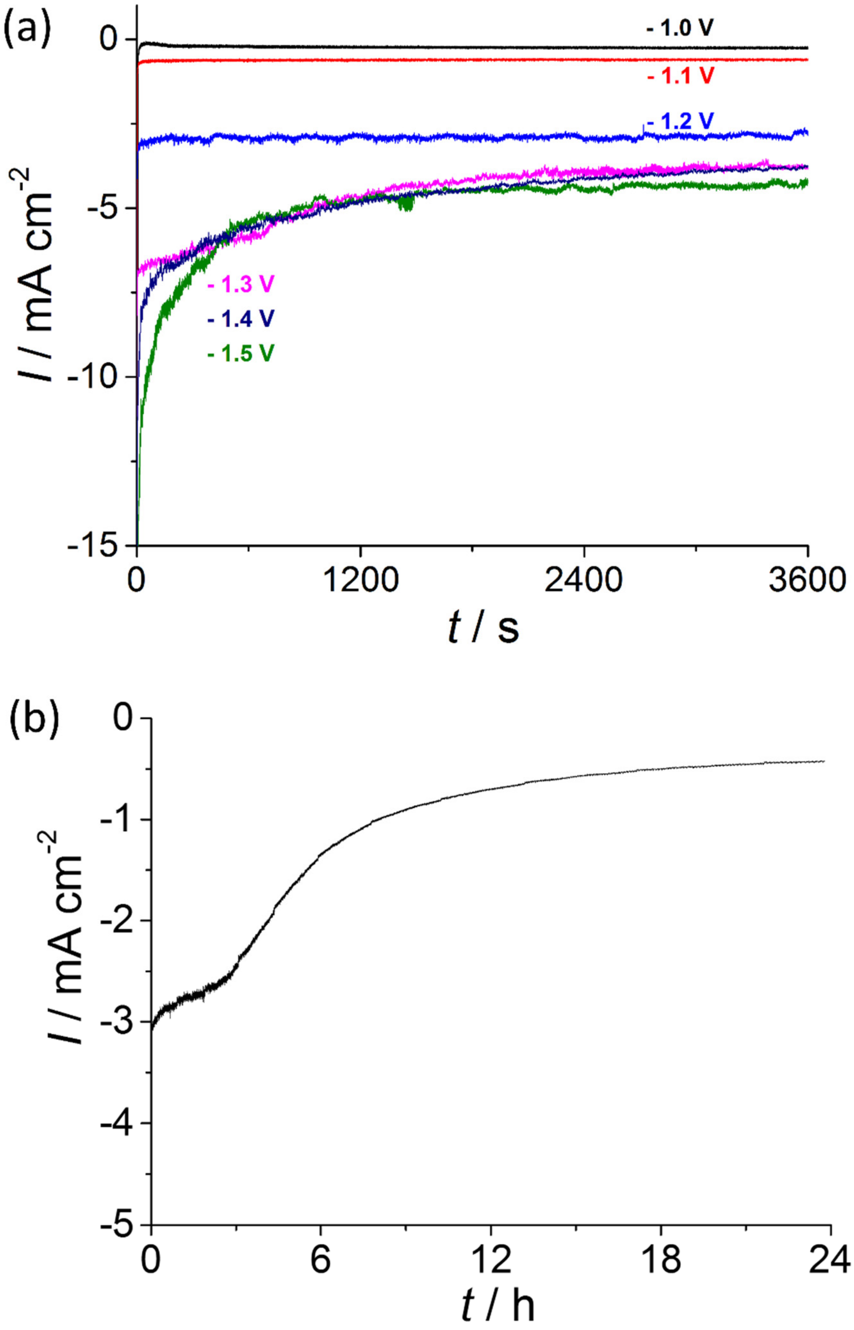

Figure S3 (a) Controlled potential electrolysis of electroreduction of CO_2 by nanoporous Ag performed at potentials between -1.0 V and -1.5 V (vs Ag/AgCl (3M NaCl)) in seawater. (b) The current-time profile over a 24 h electrolysis at -1.2 V in seawater.

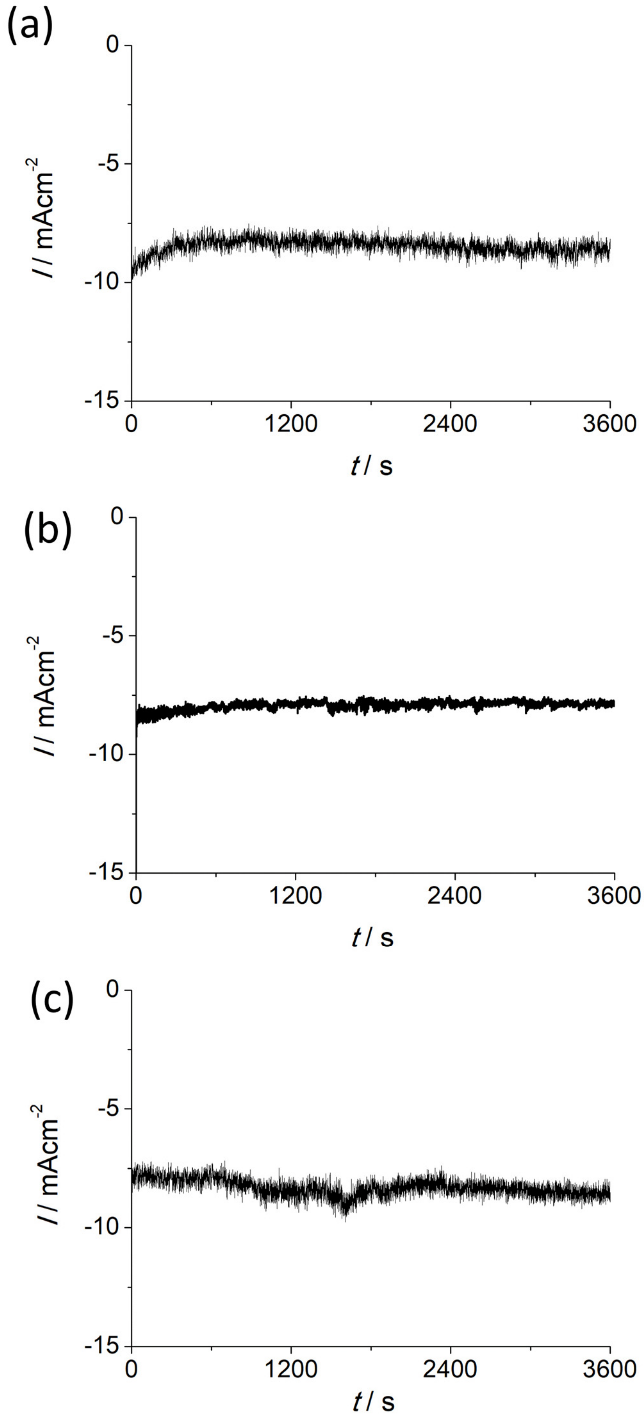

Figure S4 Controlled potential electrolysis of electroreduction of CO_2 by nanoporous Ag performed at -1.4 V ((vs Ag/AgCl (3M NaCl)) in 3.5 wt % NaCl with the presence of 20 mM of K^+ (a), Mg^{2+} (b) and SO_4^{2-} (c). Unlike the Ca^{2+} case (see Figure S3), the currents remained stable, and the calculated faradaic conversion efficiencies of CO_2 to CO are above 90 %.

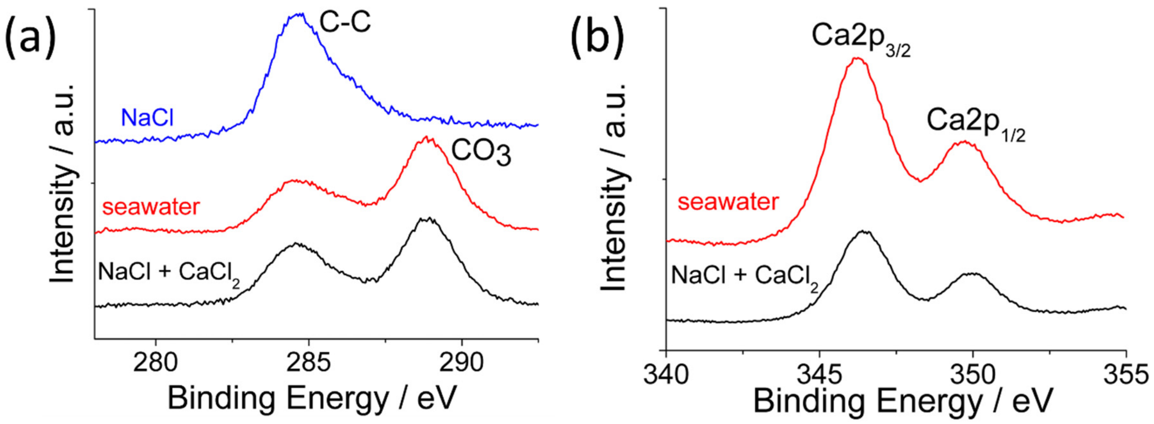

Figure S5 XPS spectra of (a) C and (b) Ca2p of the as formed Ag/AgCl; the nanoporus Ag (np-Ag) formed by electroreduction of AgCl; the np-Ag after undergone electrolysis in seawater and 3.5 wt % NaCl in the presence of 20 mM $CaCl_2$, respectively.

The binding energy of a standard C 1s peak (Figure 2e(ii)) at 289.3 ± 0.2 eV corresponded to CO_3 in the $CaCO_3$ surface, and the adventitious carbon peak occurred at 284.6 eV derived from contamination of the samples upon exposure to air. Furthermore, the high-energy resolution of the Ca (2p) spectra of the $CaCO_3$ samples indicated two binding energies for Ca $2p_{3/2}$ and Ca $2p_{1/2}$, as shown in Figure 2e(ii).[3]

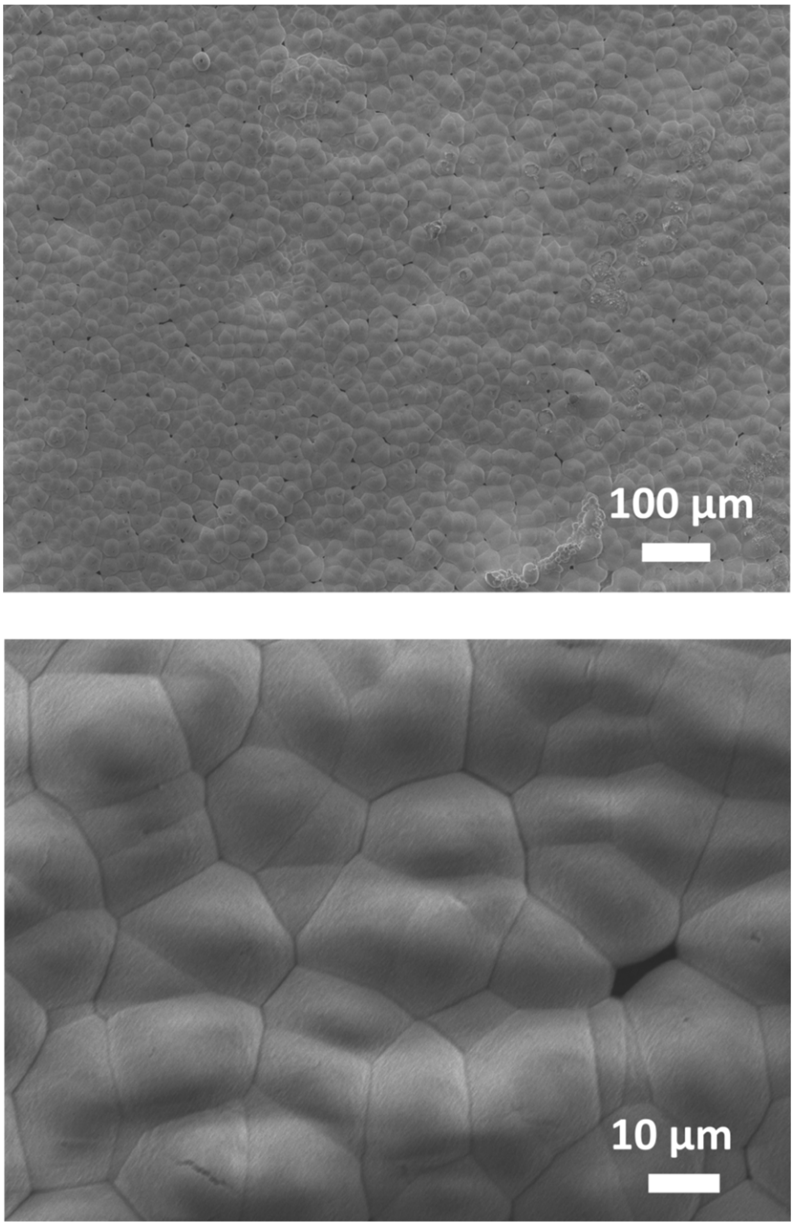

Figure S6 SEM images of the Ag/AgCl electrode after electroreduction of CO_2 to CO at -1.4 V (vs Ag/AgCl (3M NaCl)) in seawater for 16 h.

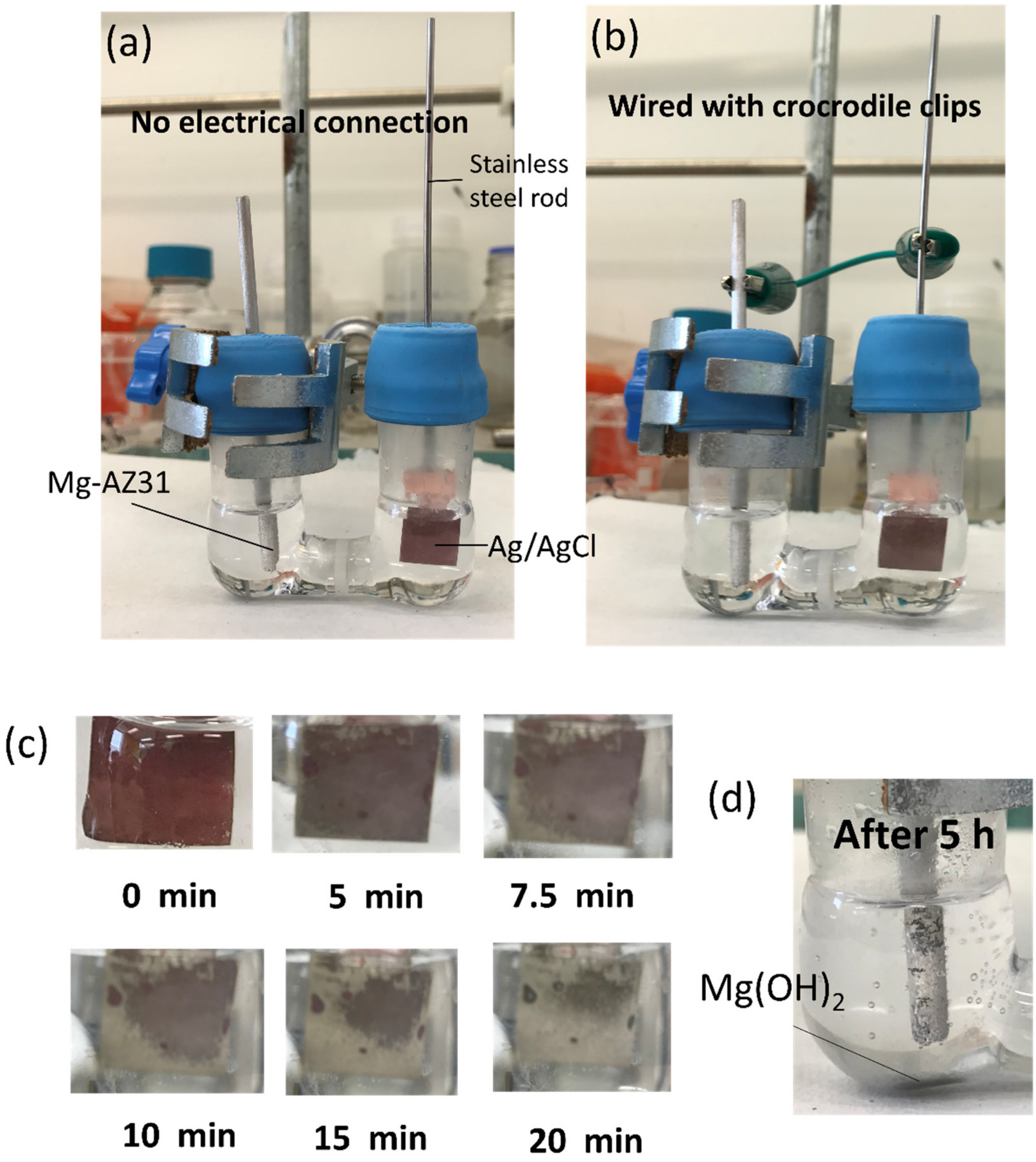

Figure S7 Optical images of a typical glass frit-based two-compartmented self-powered cell assembly before (a), and just after (b) electrical connection made by wiring a Mg-AZ 31 anode and a Ag/AgCl cathode using crocodile clips. The employed electrolyte was seawater, and the cathodic compartment was purged and saturated with CO_2 prior to experiment. (c) Upon electrical connection was established, the spontaneous oxidation of a Mg-AZ 31 generated electrons for electroreduction of AgCl to nanoporous Ag film. The initially brownish AgCl film became faded, gradually changed to silver-grey colour as shown with images taken at different time intervals. The highly active reduced Ag (at 25 min) in conversion of CO_2 to CO can be seen in Video S1. (d) An optical image shows the precipitation of $Mg(OH)_2$ as a by-product from anodic dissolution of Mg alloy.

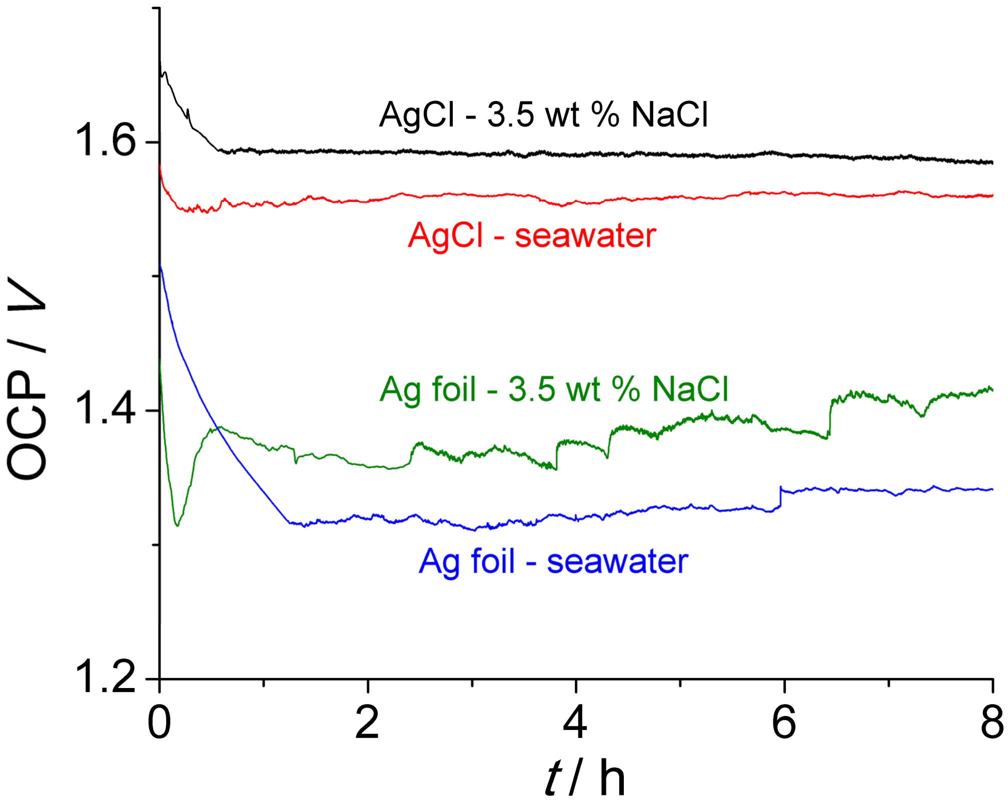

Figure S8 The open circuit potential *vs.* time for Ag/AgCl and bare Ag foil performed at a two-compartment cell. Mg alloy was in the anodic compartment, with the electrolyte was either a 3.5 wt % NaCl or seawater.

After an initial OCP drop in the first hour, the assembled cell with a Ag/AgCl electrode shows a stable OCP trend over the 8 h in both 3.5 wt % NaCl and seawater. When Ag foil was employed, a lower OCP of ~ 1.4 V was achieved, and a lesser stability indicates the role of formation of AgCl on Ag as a protective layer.

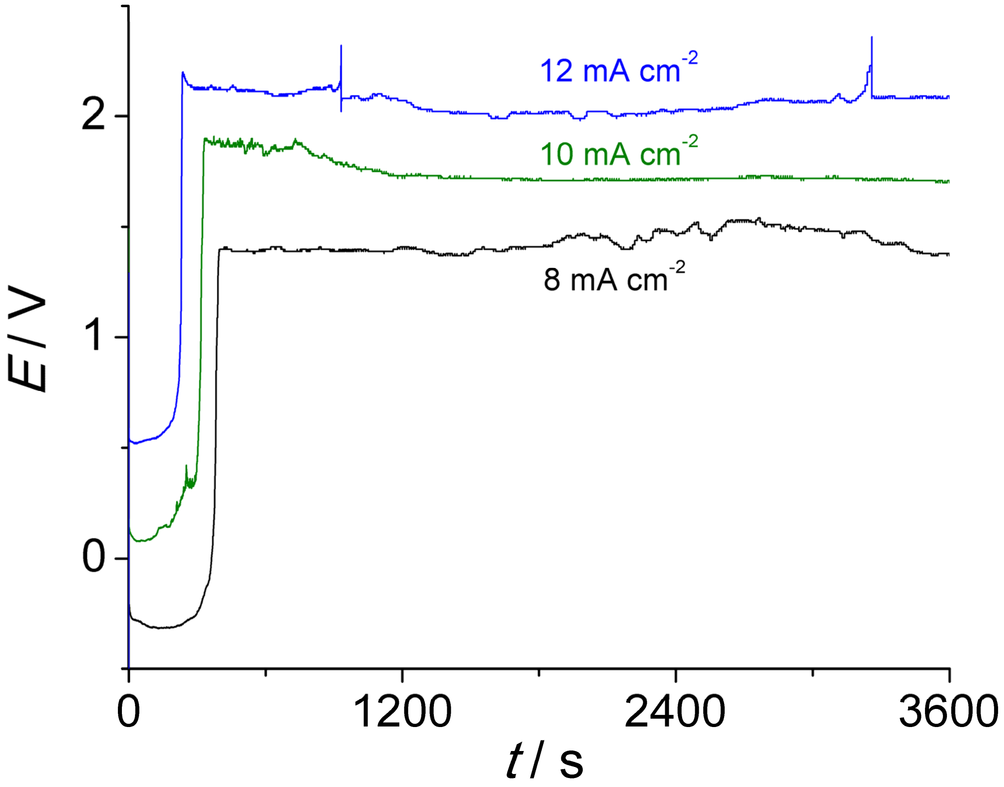

Figure S9 Chronopotentiometry measurement performed at the fixed current densities of 8, 10 and 12 mA cm^{-2} in 3.5 wt % NaCl, performed in a two-electrode system with a Ag/AgCl electrode as a working electrode, and a Mg alloy as the counter electrode, respectively.

Upon discharge the cell with the applied fix current densities at the cathode, the voltage increased gradually due to the electroreduction of AgCl, and then reaching a maximum voltage when AgCl was being fully reduced to nanoporous Ag. This reductive process can be followed visibly through gradual change of electrode's colour from brownish to silver-grey. A higher applied current density promoting faster reduction to Ag, and enhanced cell voltage.

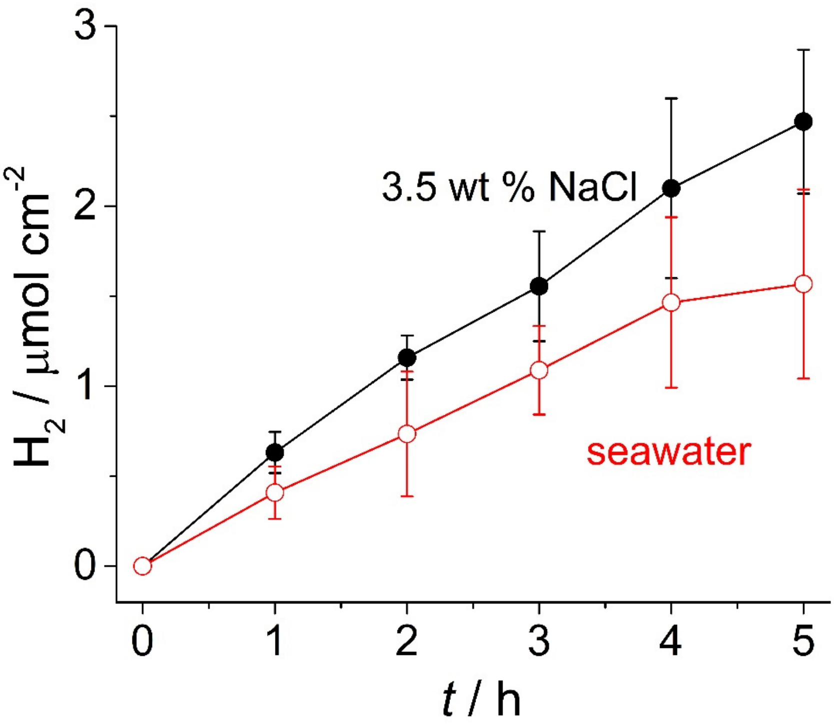

Figure S10 Plot of mole of H_2 obtained from the cathodic compartment with nanoporous Ag as a catalyst, over 5 h self-powered full-cell assembly in 3.5 wt % NaCl and seawater.

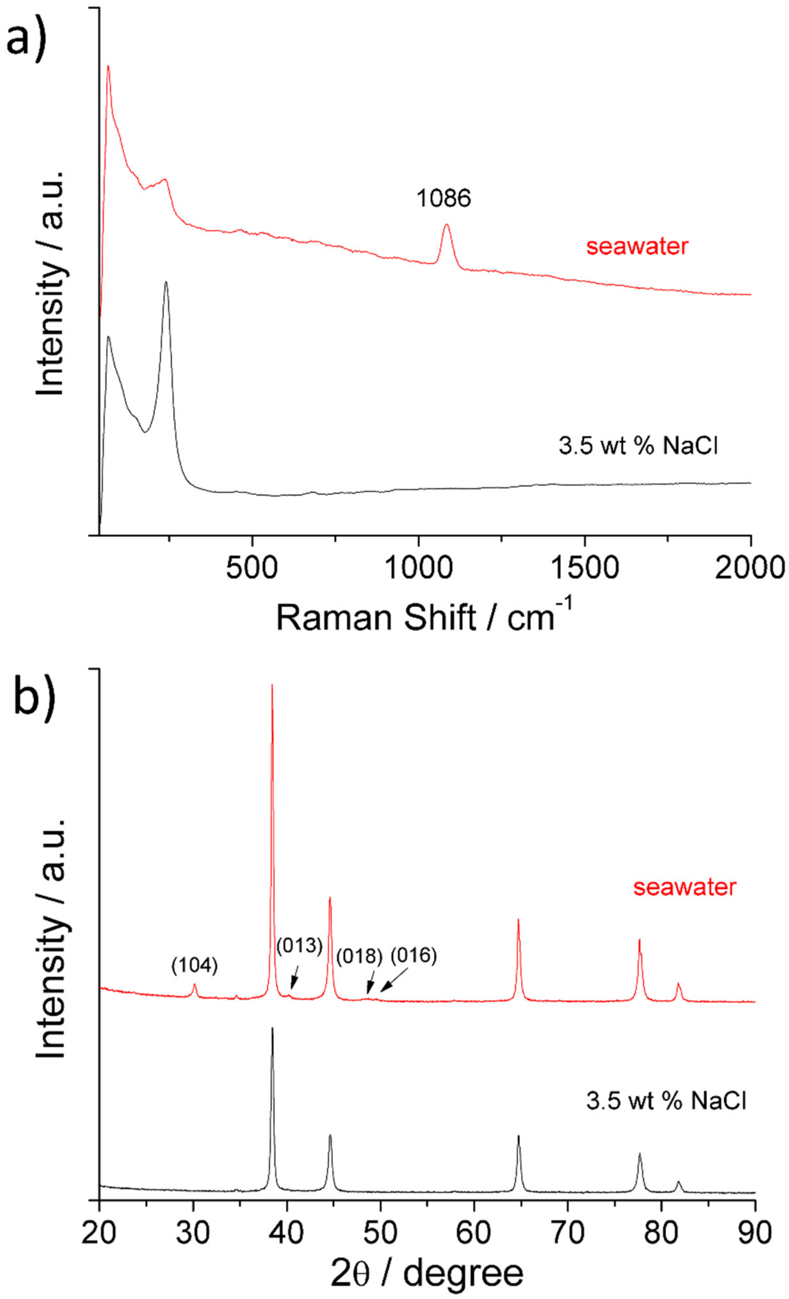

Figure S11 (a) Raman and (b) XRD data of the Ag/AgCl electrodes employed in a self-powered full-cell assembly in electrolyte containing 3.5 wt % NaCl and seawater. The formation of calcite is evidenced in the electroreduced Ag in seawater.

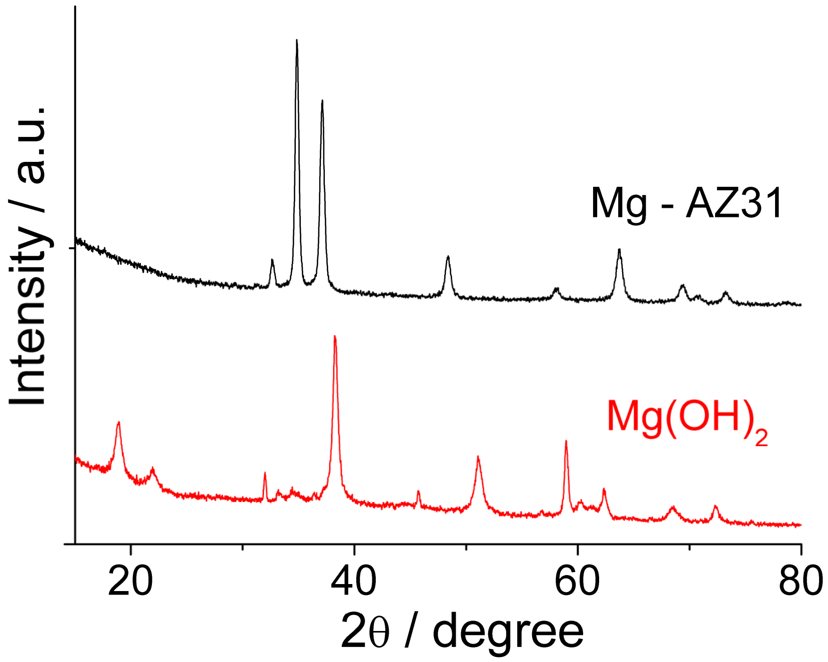

Figure S12 XRD patterns of a Mg alloy (Mg - AZ31) and the obtained by-product, $Mg(OH)_2$ after the spontaneous anodic dissolution to generate H_2.

Video S1

Video of the reported self-powered system with a Mg-AZ31 anode wired to a Ag/AgCl cathode (after self-powered AgCl electroreduction at 25 min – please see Figure S6 for further information). The Ag/AgCl cathodic compartment with seawater as an electrolyte was pre-purged and saturated with CO_2 prior to the experiment. Both anode and cathode generated gases; this video provides a closer look at the highly active reduced Ag in converting CO_2 to CO, with the released of CO gas bubbles from the electrode surface.

References

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[2] Y. Zhao, C. Wang, G. G. Wallace, *J. Mater. Chem. A***,** 2016, **4**, 10710-10718

[3] M. Ni, B. D. Ratner, *Surf. Interface Anal.* 2008, **40**, 1356-1361.