Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Electronic Supplementary Information

Solar Demonstrator Device for Brine Splitting

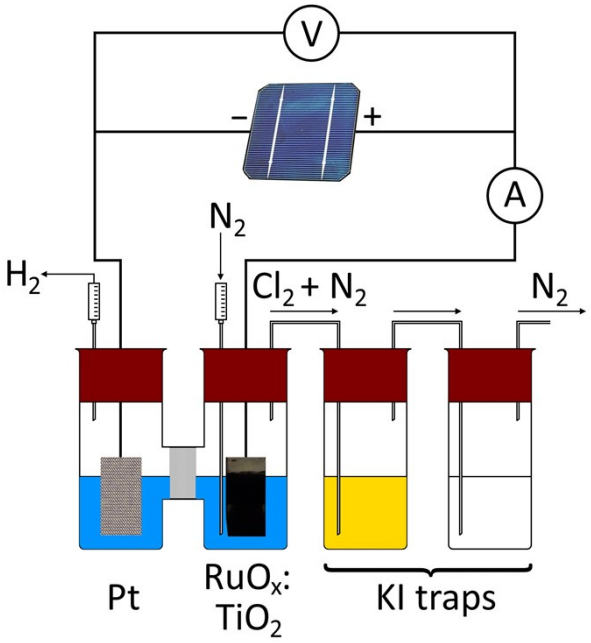

Figure S1: Schematic of the demonstrator device for the photocleavage of brine. Platinum mesh was used as the cathode while the anode was compromised a thin film of the best performing ClOC sample (50 at% Ru) on FTO glass. Cl_2 production was measured using a KI trap and H_2 production was measured using gas chromatography and changes in current. The device was powered using an amorphous Si solar cell.

A full schematic of the solar demonstrator device is shown in Figure S1. The demonstrator device was powered using amorphous silicon solar cells (Sanyo AM-5302, Maplin, London, UK). The solar cell consisted of an array of 6 cells, which produce a short-circuit current of 105 mA and open-circuit voltage of 2.5 V under AM 1.5 solar irradiance (100 $mW.cm^{-2}$). A simple desk lamp (Bobby Desk Lamp, Habitat, London, UK), equipped with a 40 W halogen bulb, was used to irradiate the solar cell, resulting in an operating current and voltage of 4.8 mA and 1.89 V, respectively. Experiments were conducted in a gas-tight, two compartment glass cell, separated with a salt ion exchange membrane. The anode consisted of a thin film of the spin coated sample R50T50 on NSG TEK-15 FTO glass. The cathode consisted of a platinum mesh. The electrolyte was 0.5 M H_2SO_4(aq) + 2.0 M NaCl(aq) (pH ~ 0.56). Suba-seals™ were used to create a gas-tight atmosphere within the cell. Wires were placed through the centre of each

Suba-seal® with a crocodile clip attached to each electrode. The area of each electrode submerged in the electrolyte was adjusted to ~ 1 cm^2. Currents and voltages were measured using digital multimeters (MY64, Mastech Instruments, California, USA). A gas chromatograph (Varian CP-3800) was first calibrated using a range of dilutions, from 0 to 5 %, of 5 % H_2: 95 % N_2 gas. The amount of hydrogen produced at the platinum cathode of the demonstrator device was measured using gas chromatography by injecting 250 µL gaseous aliquots of headspace, at select times, through a column packed with molecular sieves (80-100 Mesh). The amount of chlorine gas produced at the RuO_2:TiO_2 anode of the demonstrator device was measured using a KI trap. UV-visible absorption spectra of the KI trap solution was measured at the end of each experiment to determine the chlorine yield.

Measured Gas Evolution

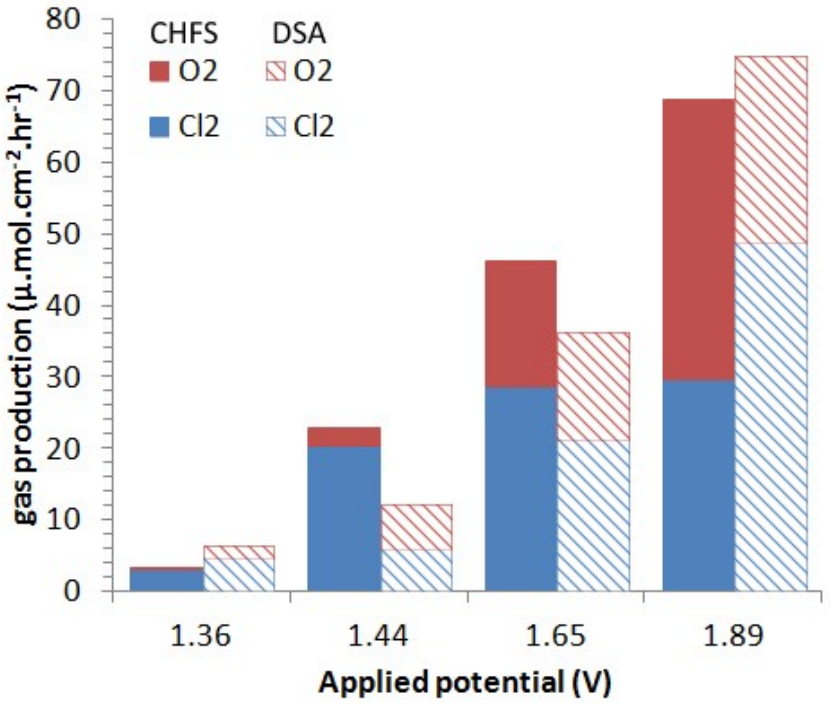

Figure S2: Chlorine (blue) and oxygen (red) gas evolution measured at applied potentials of 1.36, 1.44, 1.65 and 1.89 V, respectively. CHFS-made ruthenium-titanium oxides (solid) and DSA-type (hash) materials deposited on FTO glass were tested independently. Chlorine gas was measured using a KI trap to produce triiodide (I_3^-) that can be measured using UV-visible spectroscopy, oxygen production is assumed to form the remainder of the gas evolved. The device was powered using a potentiostat.

DSA-Type Anode Preparation

To produce DSA-type films, a suitable precursor solution was produced, this consisted of; 2.86 g ruthenium chloride hydrate, $RuCl_3 \cdot 0.5H_2O$, 4.5 mL tetrabutyl titanate, $Ti[(OCH_2)_3CH_3]_4$, 0.6 mL hydrochloric acid and 9.3 mL butyl alcohol, $CH_3(CH_2)_3OH$. The solution was stirred and brush coated on to fluorine doped tin oxide (FTO) glass. Thermal conversion of was carried out by drying the solution at 100 ˚C (ramp rate 5 ˚C.min^{-1}) and held for 15 min followed by further heat treatment at 450 ˚C (ramp rate 10 ˚C.min^{-1}) and held for 30 min, before being removed from the furnace and left to cool. The process was repeated 5 times to obtain a suitable catalyst loading on the FTO substrate.