

Supporting Information

EQCM Investigation of Electrochemical Deposition
and Stability of Co-Pi Oxygen Evolution Catalyst of
Solar Energy Storage

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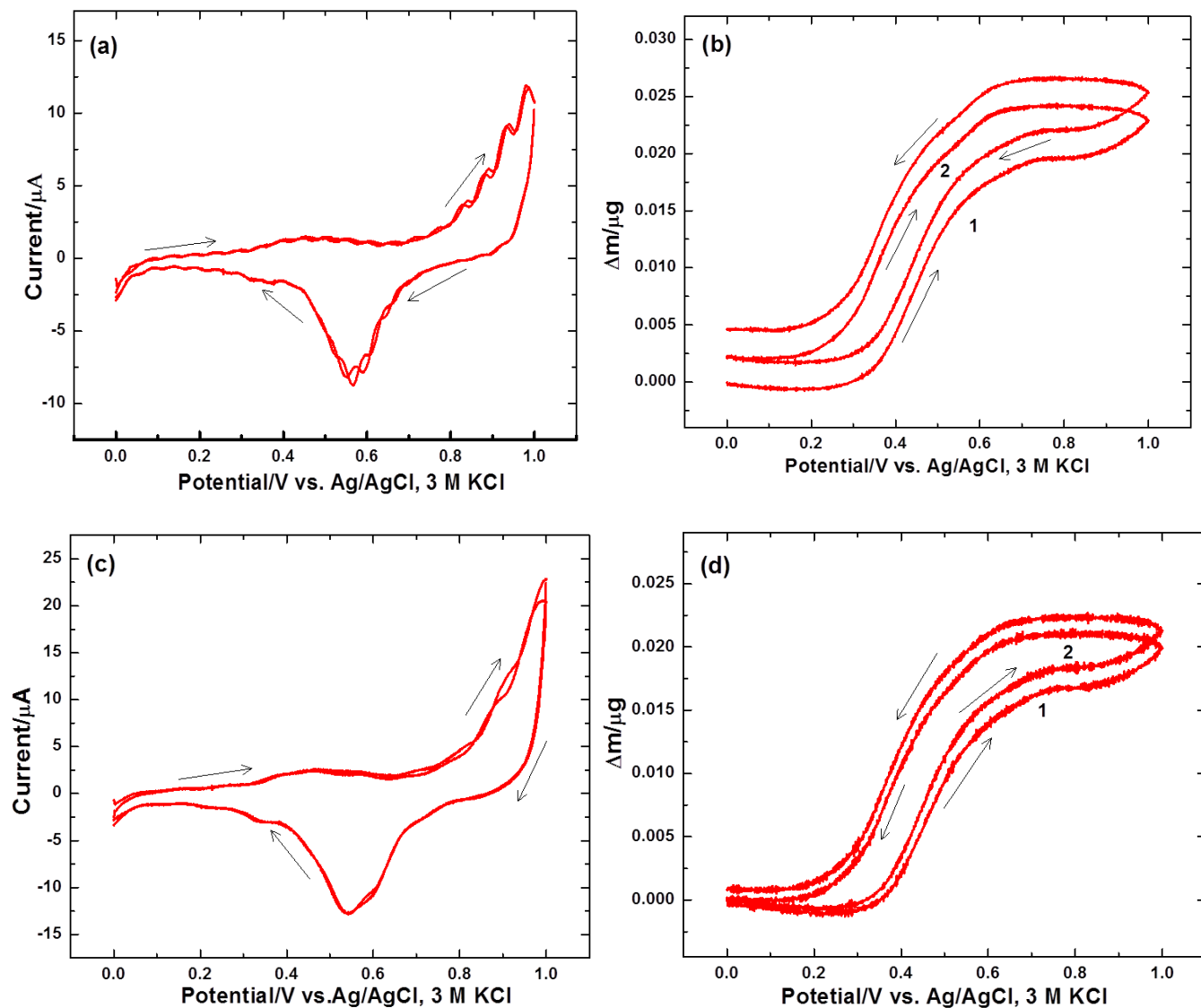


Figure S1:(a and c) Cyclic voltammograms and (b and d) mass variation (Δm) vs. potential of Au coated quartz crystal in 0.1 M Phosphate buffer (pH 7) at a sweep rate of (a and b) 25 mVs⁻¹ and (c and d) 50 mVs⁻¹. Area of the Au electrode is 0.205 cm².

Measurement of motional resistance:

The figures presented below suggest that the motional resistance of the quartz crystal measured as a function of potential, time and mass of the deposit is nearly invariant.

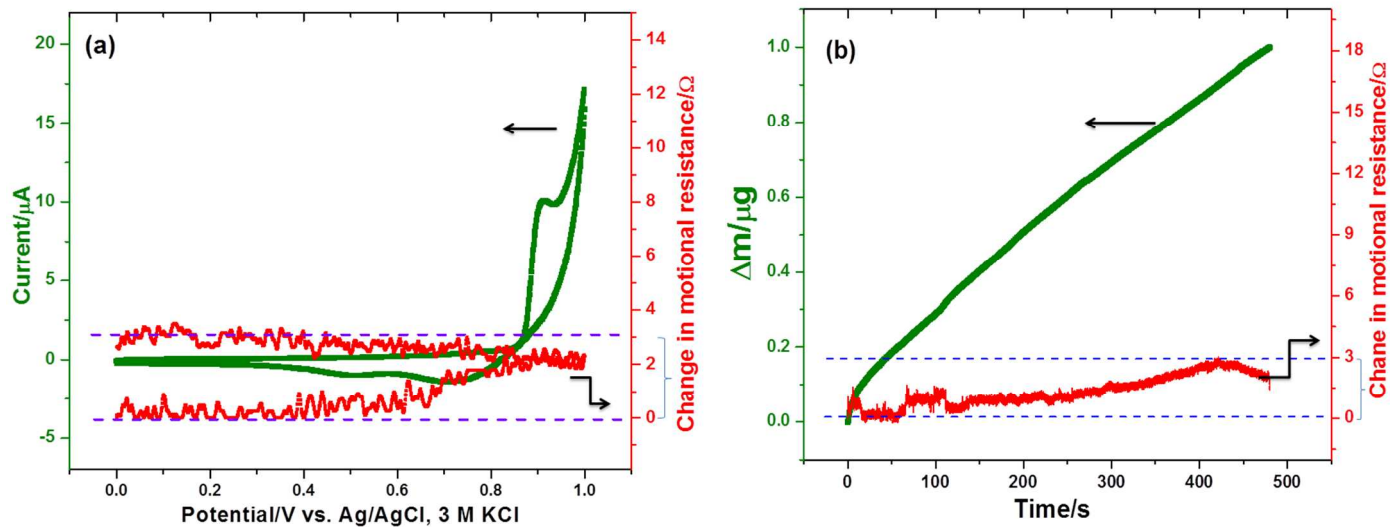


Figure S2:(a)Current (green) and motional resistance (red) variations with potential during cyclic voltammetry experiments at 5 mVs^{-1} using Au coated quartz crystal(area 0.205 cm^2)in 0.1 M phosphate buffer (pH 7) containing 0.5 mM Co^{2+} . (b) Variations in mass (green) and change of motional resistance (red) with time of Co-Pi catalyst depositionat 1.00 V.

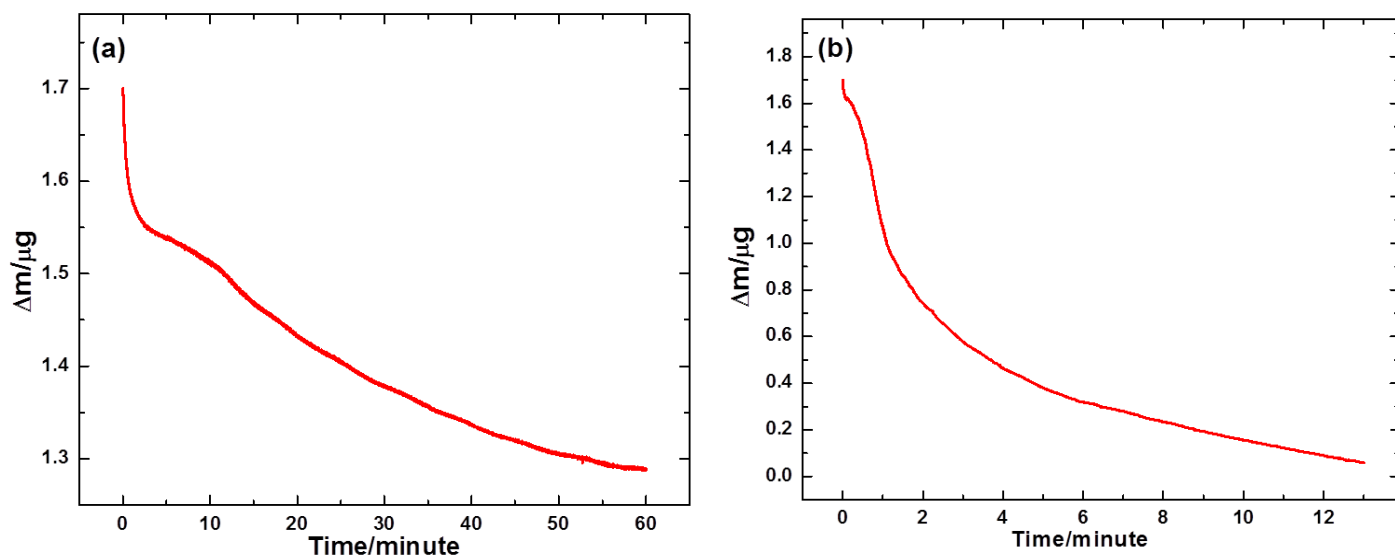


Figure S3: Mass variation of Co-Pi coated (1.7 μg) Au coated quartz crystal electrode during electrolysis in 0.1 M K_2SO_4 at (a) 0.60 and (b) 1.60 V.

Tafel Experiments:

The superior performance of the in-situ formed Co-Pi catalyst on Au surface was evidenced from slow scan rate (0.05 mV s^{-1}) linear sweep voltammograms and Tafel plots measured under stirring condition (Fig. S3). Current density of about 2 mA cm^{-2} was observed at 1.10 V in neutral phosphate buffer containing Co^{2+} (Fig. S3 curve i) whereas it requires more than 1.36 V to attain the same current density in the absence of cobalt salts (Fig. S3 curve ii). It is also found that the deposited Co-Pi catalyst retains comparable OER activity even in non-cobaltous solution (Fig. S3 curve iii), suggesting catalytic activity of Co-Pi in the absence of Co^{2+} in buffer solution. Linear regime of the Tafel plot (inset in Fig.S3) provides a slope of 94 and 150 mV per decade, respectively in non-cobaltous and cobaltous solutions. Tafel slope for Co-Pi/Au electrode in 0.1 M phosphate buffer containing no Co^{2+} was 109 mV per decade, which is close to the literature value (100 mV per log unit) for Co-Pi film/Co system.^{S1}

References:

S1: Young, E. R.; Nocera, D. G.; Bulovic, V. Direct Formation of a Water Oxidation Catalyst from Thin-film Cobalt. *Energy Environ. Sci.* **2010**, *3*, 1726-1728.

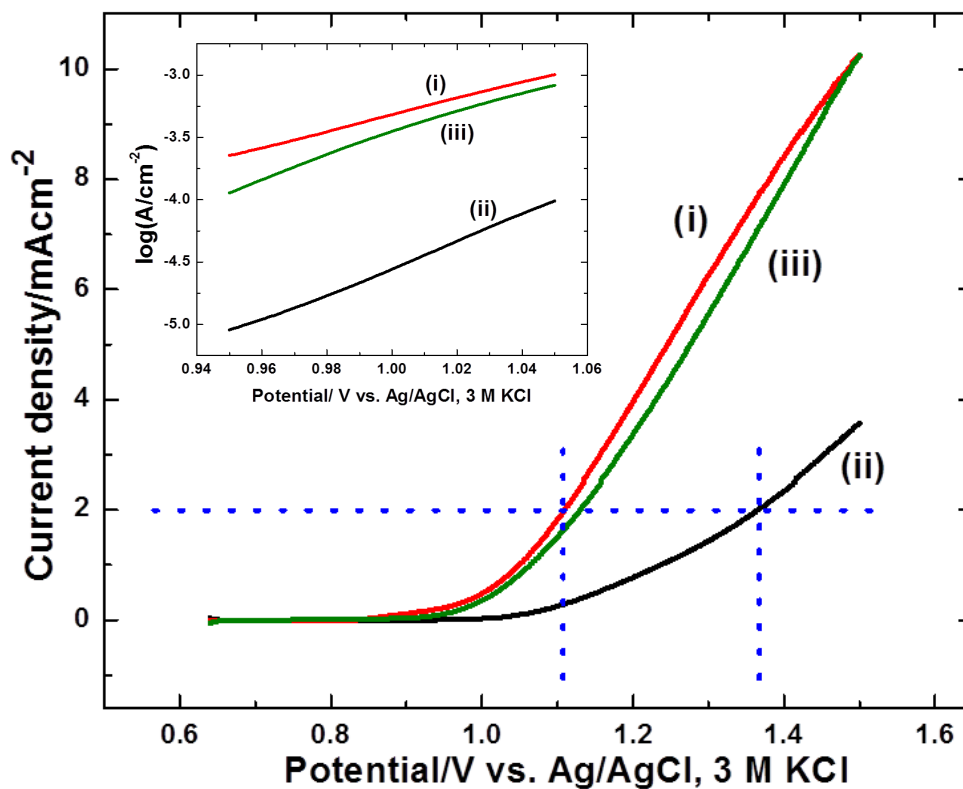


Figure S4: Linear sweep voltammograms of Au electrode (1cm^2) at 0.05 mV s^{-1} in 0.1 M neutral phosphate buffer (i) with 0.5 mM Co^{2+} (ii) without Co^{2+} and (iii) linear sweep voltammograms using Co-Pi deposited (20 C cm^{-2}) Au electrode in 0.1 M phosphate buffer without Co^{2+} . Inset shows the linear regime of the corresponding Tafel plots.