Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic supplementary information

Oxygen Evolution Co-Ac Catalyst - Synergistic Effect of Phosphate Ion

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S1: Electrochemical stability of acetate buffer on Pt electrode

Electrochemical stability of neutral acetate electrolyte under oxygen evolution condition is analysed by cyclic voltammetry experiment in 0.1 M acetate buffer solution using a Pt foil electrode. It is seen in Fig. S1 that any significant diffusion controlled current peaks corresponding to acetate oxidation are absent in the potential region of the present study.

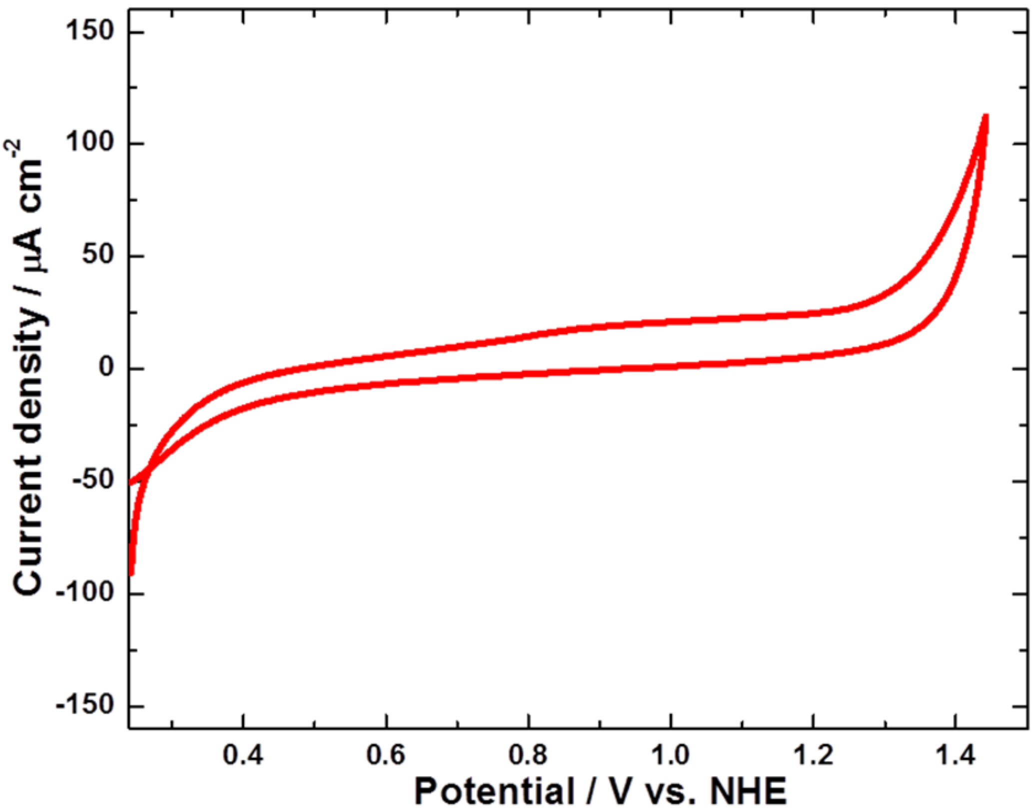

Fig. S1: Cyclic voltammograms of a Pt foil electrode in 0.1 M acetate buffer (pH 7.0). Sweep rate: 5 mV s^{-1}.

S2: Detection of oxygen using ORR on Pt

The evolved oxygen during water oxidation on Co-Ac catalyst was probed on a Pt electrode utilizing its high catalytic activity towards oxygen reduction reaction (ORR). An air-tight electrochemical cell consists of a well cleaned Pt foil and Co-Ac catalyst (5 C cm^{-2}) deposited carbon paper electrode as the working electrodes for ORR and OER respectively. Saturated calomel electrode and another Pt foil electrode were used as reference and counter electrodes. The glass cell was filled with acetate buffer electrolyte and thoroughly purged with high purity Ar-gas for 3 h with stirring to remove dissolved oxygen. Then, the Pt electrode was swept from 0.45 to -0.35 V at 50 mV s^{-1}. Negligibly small current flows (Fig. S2 (i)). Then, electrolysis was conducted at Co-Ac loaded carbon paper electrode by applying a constant potential of 1.35 V. After 1 h, electrolysis was terminated and Pt was swept from 0.45 to -0.35 V (Fig. S2 (ii). A current peak appears at about -0.025 V. Into the same electrolyte, pure O_2 gas was bubbled from a cylinder for about 1 h and again Pt electrode was subjected to linear sweep voltammetry. The reduction current peak at -0.025 V increases in magnitude. These studies confirm that the electrolysis product evolving at Co-Ac anode was oxygen. The cathodic current peak observed at Pt electrode is due to the reduction of O_2.

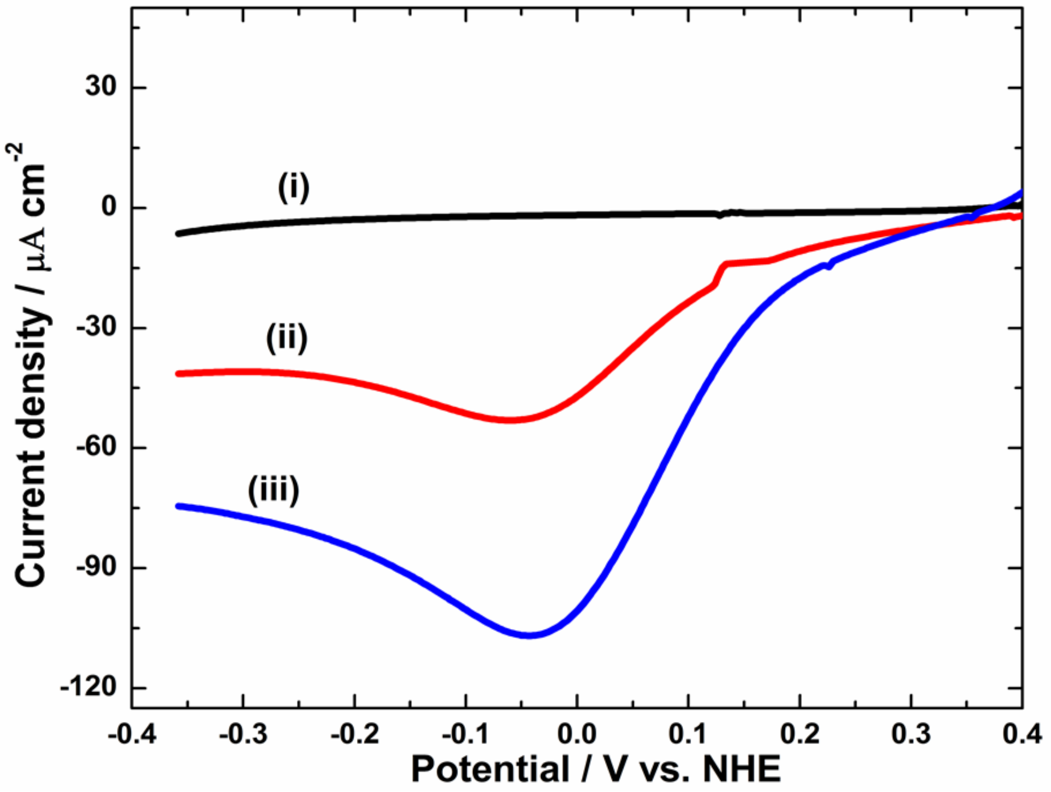

Fig. S2: Linear sweep voltammograms of Pt electrode in 0.1 M acetate electrolyte under (i) Ar-saturated condition, (ii) after 1 h of oxygen evolution reaction at 1.35 V on Co-Ac deposited carbon paper electrode and (iii) after purging with O_2. Sweep rate: 50 mV s^{-1}.

S3: Effect of acetate ion concentration

Oxygen evolution activity of Co-Ac catalyst was measured both in 0.1 M and 1.0 M acetate buffer electrolytes. For this, Co-Ac was deposited on carbon paper electrode at 1.30 V for 1 h from 0.1 M acetate solution containing 0.5 mM Co^{2+}. Electrodes were washed well with water and dried in vacuum. The electrode was then transferred to electrolyte under study and linear sweep voltammograms were recorded at 5 mV s^{-1} (Fig. S3). It is observed that current density in the potential of range of our studies is independent of acetate ion concentration.

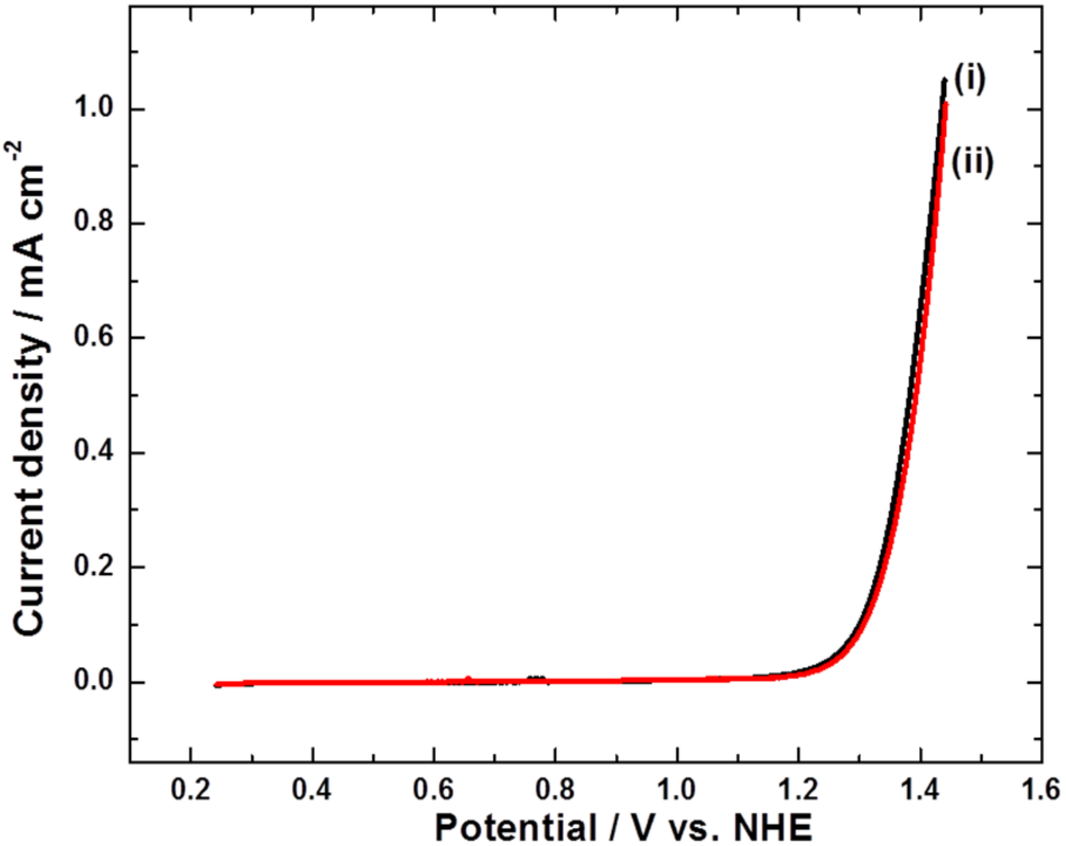

Fig. S3: Linear sweep voltammograms of Co-Ac deposited carbon paper in (i) 1.0 M and (ii) 0.1 M acetate buffer solutions. Sweep rate: 5 mV s^{-1}.

S4: Stability of Co-Ac catalyst in phosphate buffer electrolyte

Stability of the Co-Ac catalyst was studied by bulk electrolysis for 24 h in phosphate buffer solution. For this, Co-Ac was deposited at 1.30 V for 1 h from 0.5 mM Co^{2+}+ 0.1 M acetate solution. The electrode was rinsed with double distilled water and dried overnight in vacuum. The electrode was then transferred to 0.1 M phosphate electrolyte (pH 7.0) and subjected to electrolysis at 1.30 V for 24 h under stirring condition. As shown below in Fig S4, there is a gradual increase in the current during the initial stage of electrolysis. It could be due to the formation of a more active hybrid Co-Ac-Pi catalyst. After 5 h, the current reaches a steady value of 0.40 mA cm^{-2}. The current value maintains at around 0.35 mA cm^{-2} even after 24 h of electrolysis indicating a high stability of the catalyst material under water oxidation condition.

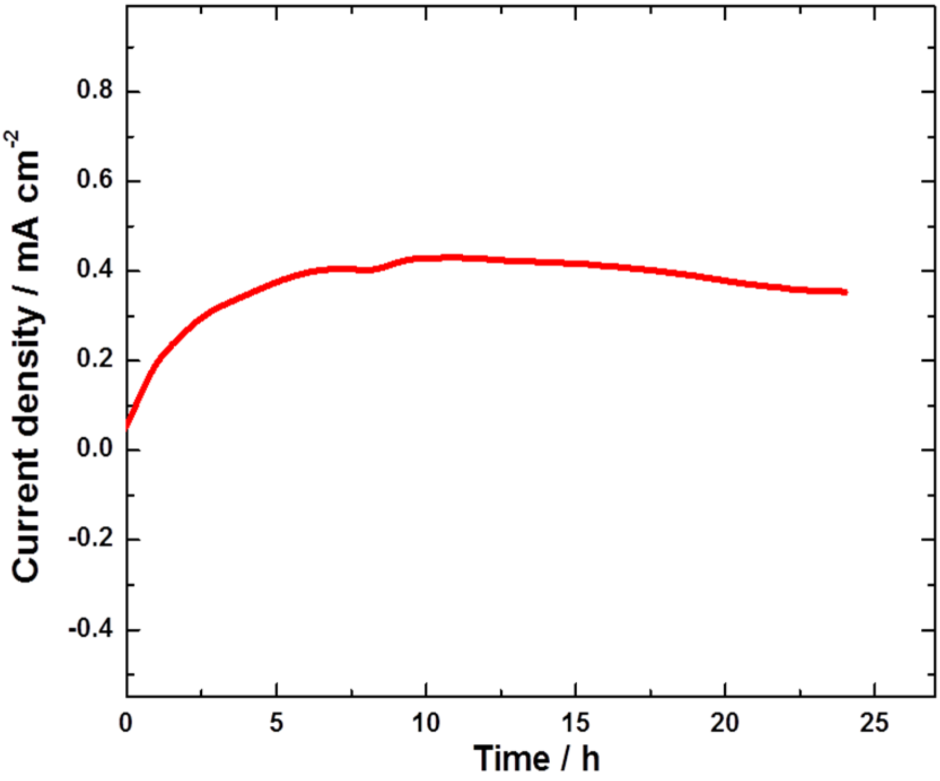

Fig. S4: Stability data for the Co-Ac catalyst during constant potential electrolysis at 1.30 V for 24 h in a neutral phosphate buffer electrolyte.

S5: Powder X-ray diffraction

XRD patterns were recorded for bare carbon paper substrate and for Co-Ac catalyst deposited carbon paper electrode (Fig. S5). The pattern for the substrate consisted of peaks at $2\theta = 26.2$ and 54.4° due to carbon crystallites. Only these reflections were identified even after the catalyst deposition, indicating amorphous nature of Co-Ac catalyst.

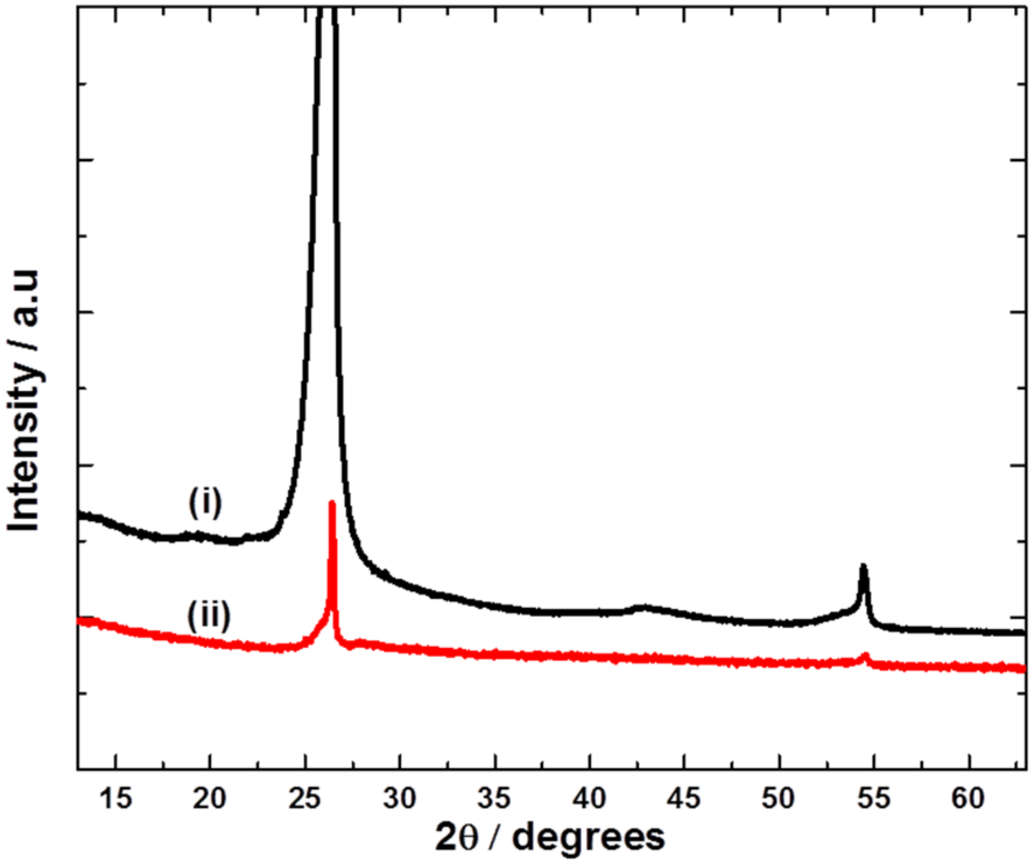

Fig. S5: XRD pattern of carbon paper electrode (i) before deposition and (ii) after Co-Ac catalyst deposition. Co-Ac was deposited at 1.30 V from 50 mM Co^{2+}+ 0.1 M acetate until 35 C cm^{-2} charge was passed.