# Supporting Information

# An Acetate Bound Cobalt Oxide Catalyst for Water Oxidation: Role of Monovalent Anions and Cations In Lowering Overpotential

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## **General Procedures**

All the starting materials are purchased from Merck Chemicals Ltd, India through vendors and are used without further puridications. The indium doped tin oxide (ITO) and fluorine doped tin oxide electrodes are purchased from Sigma-Aldrich India and are used after cleaning. The slicon-carbide electrode was directly extracted from market available batteries and washed thoroughly with concentrated HNO<sub>3</sub> and water and dried for overnight for further use. For all the experiments triple distilled water is used. The electrochemical measurements have been performed with Pine CHI 720D bipotentiostate using a Pt wire counter electrodes (CHI 115) and Ag/AgCl (sat. KCl) reference (CHI 111) electrodes. FTIR spectra is recorded in Perkin-Elmer Frontier model using ATR technique. Field-emission scanning electron microscopy (FESEM) was performed with model JEOL JSM-6700F) and high-resolution transmission electron microscopic (HRTEM) topographs are collected from a JEOL-JEM 2010 microscope using 200k eV electron source. Energy-dispersive X-ray spectroscopy (XPS, Omicron, model: 1712-62-11) measurement was done using an Al-Ka radiation source under 15 kV voltage and 5 mA current condition.

Figure S1: Determination of overpotential  $(\eta)$  by extrapolating the faradic current curve. (A) Homegeneous & (B) Heterogeneous.



Figure S2 : Cyclic Voltamogram of (A) 5 mM solution of the transition metal salts with GC electrode and (B) with ITO electrode modified with the Ni-Ac-WOC, Fe-Ac-WOC, Mn-Ac-WOC and comparison with Co-Ac-WOC at 50 mVs<sup>-1</sup> scan rate in acetate buffer (pH 7).



### **Detection of O2 Evolved**

The O<sub>2</sub> evolved during OER is detected using electrochemical methods.

### A) Homogeneous

During an anodic liner sweep of an edge-pane graphite working electrode mounted on a rotor tip of a RRDE assembly and dipped in a solution of 5 mM Co<sup>2+</sup> ions in acetate buffer with KCl electrolyte, the encircling Pt ring is held at a constant potential of -0.2 V vs NHE. At this potential Pt ring electrochemically reduces O<sub>2</sub>. As an anodic current is observed in the working electrode a reduction current is also observed at the ring (Fig. S3A, left). Thus O<sub>2</sub> produced at the working disc electrode (H<sub>2</sub>O  $\rightarrow$  2H<sup>+</sup> + 4e + ½ O<sub>2</sub>) it diffuses out towards the ring due to the hydrodynamic current produced by the rotating shaft and gets reduced. To eliminate the possibility that this reduction current may also originate from an oxidized Co species, produced at the anode at positive potentials and diffused towards the ring, getting reduced in a manner analogous to O<sub>2</sub>, the RRDE experiment is performed by holding the Pt electrode at several different potential. The current vs potential plot of such an experiment profiles the O<sub>2</sub> reduction current of the ring very closely (Fig. S3B, right). These data strongly indicates that the current produced at the ring is due to reduction of O<sub>2</sub> produced at the working disc electrode.

Pic S1: Electrochemical set up for heterogeneous  $O_2$  detection, generated by the Co-Ac-WOC on ITO/FTO electrode.



### B) Heterogeneous

In a standard two compartment cell, an auxiliary Pt electrode, in addition to the working electrode bearing deposits of Co-Ac-WOC and the reference electrode, a Pt electrode is introduced (see picture below). After performing CPE experiments at 0.95 V vs NHE (i.e. with ~120 mV overpotential) in a degassed buffered solution with the working electrode for different spans of time, the auxiliary Pt electrode, now used as a working electrode, is used to reduce any  $O_2$  present in the solution. The data (Fig. S2D) indicate that while initially no  $O_2$  reduction currents are observed, significant  $O_2$  reduction currents are observed as the CPE proceeds. In particular the amount of  $O_2$  reduction current increases with increasing CPE time. This clearly indicates generation of  $O_2$  at the working electrode at these low potentials. The generation of the  $O_2$  was confirmed by the formation of Mb- $O_2$  complex, characterized by UV-Vis spectroscopy under anaerobic condition and by subsequent addition of the small aliquot (10 µL) to the reduced Mb solution of known concentration after 20 minutes of intervals with the progress of CPE.

Figure S3: A)  $O_2$  detection under homogeneous conditions using RRDE (left). 5 mM Co<sup>2+</sup> solution in acetate buffer with KCl electrolyte at 1500 rpm and 50 mV/s. (B) Pt ring currents obtained by applying different potential at the ring during RRDE is plotted (red squares) against potential at which the ring is held. Overlaying these points is an LSV scan (in blue) of the Pt ring in an aerated acetate buffer with KCl electrolyte containing 5 mM Co<sup>2+</sup> salt. The ring currents obtained in these different RRDE experiments profile the ORR current of Pt clearly indicating that these RRDE currents are generated by  $O_2$  reduction and not any side reaction at the Pt ring electrode C) Cyclic voltamogram of the FTO electrode with Co-Ac-WOC in deoxygenated Co<sup>2+</sup> free buffer (Acetate pH 7) at 50 mVs<sup>-1</sup>. Red arrow indicates the direction of the initial scan. OER & ORR stand for oxygen evolution reaction and ORR for oxygen reduction reaction. D)  $O_2$  reduction current measured by an auxiliary Pt electrode during a CPE run of a Co-Ac-WOC deposited on an FTO electrode and held at 0.95 V in an acetate buffer with KCl electrolyte and containing 1 mM Co<sup>2+</sup> salt dissolved in it. (E) UV-vis spectra of the Mb-O<sub>2</sub> complex formed by the reaction of O<sub>2</sub> generated by OER catalysis on CPE at 0.95 V with Co-Ac-WOC and reduced Mb.



Figure S4: CV with ITO electrode in 1 mM  $Co^{2+}$  solution in acetate buffer with KCl electrolyte at pH 7 at 50 mVs<sup>-1</sup>.



Figure S5: Cyclic Voltamogram with FTO electrode at 50 mVs<sup>-1</sup> with Co-Ac-WOC at pH 7 acetate buffer and overlayed with the bare FTO electrode at a  $Co^{2+}$ -free solution under same conditions.



Figure S6: SEM topographic image of the Co-AC-WOC on ITO (A) 5 minutes & (B) 30 minutes.



Figure S7: Scanning Electron Microscopy (SEM) of the Co-Ac-WOC modified ITO surface. (A) Electrolysis at 0.75 V vs NHE. (B) Electrolysis at 0.85 V vs NHE. (C) Electrolysis at 1 V. (D) Electrolysis at 1.1 V. All potentials are against NHE.



Figure S8: SEM topograph of the modified ITO surface with (A) Co-Ac-WOC and (B) electrodeposited material from Co(II)-salt in potassium acetate buffer with KNO<sub>3</sub> electrolyte (pH 7).





Figure S9: Scan rate (v) vs current (j) plot. Co-Ac-WOC film (A) on ITO, (B) on FTO.

Figure S10: CPE with FTO electrode in pH 7 acetate buffer at 1.2 V vs NHE.



Figure S11: A) Linear Sweep Voltametry (LSV) with Si-C electrodes at pH 7 and 50 mVs<sup>-1</sup>. (B) CPE at 1.2 V vs NHE in acetate buffer (pH 7) with Si-C electrode.



Figure S12: Electrocatalytic water oxidation with GC electrode and 1 mM  $Co^{2+}$  solution at pH 7 (acetate buffer). (*Inset*) Limiting current vs (scan rate)<sup>1/2</sup> plot.



Figure S13: CV in acetate buffer (pH 7) of with different precursor  $Co^{2+}$  salts at 50 mVs<sup>-1</sup> and ITO electrode.



Determination of TOF:

Turn over frequency is determined from the double layer capacitance ( $C_{dl}$ ) of the Co-Ac-WOC film modified ITO or FTO electrode.  $C_{dl}$  could easily be determined from the current density of the modified electrode where no faradic current is observed. The difference between the anodic and cathodic current at 0.25 V vs Ag/AgCl (sat. KCl) is plotted against scan rate. From the slope of this curve the double layer capacitance of the modified electrode is easily determined to be ~ 35  $\mu$ F/cm<sup>2</sup> for both ITO and FTO electrode. The active surface area for such oxide based material modified electrodes could easily be determined assuming the standard  $C_{dl}$  to be 60  $\mu$ F/cm<sup>2</sup>. Though, this value is very arbitrary, this method is widely acceptable. The TOF has been determined from the double layer capacitance of the Co-Ac-WOC surface ( $C_{dl} = 35 \mu$ F/cm<sup>2</sup>) and stredy current density (2.5 mA/cm<sup>2</sup>) which is converted to the number of electrons passed through the electrode per second. The number of electrons could be converted to number of oxygen per second by dividing with 4, as per molecule of oxygen generation involves 4 er oxidation.

Using these results, the TOF has been determined to be 17.8 s<sup>-1</sup> at 485 mV overpotentials with ITO electrodes and 7.9 s<sup>-1</sup> at 385 mV (1.07 mA/cm<sup>2</sup>) overpotentials with FTO electrodes. This is the highest limiting value as  $C_{dl}$  is the measure of the charge passed through the metal centre present at the surface only. So, the actual number of metal centers participating in the catalysis may be larger.

In parallel the amount of  $O_2$  gas evolved during an analogous CPE experiment at 0.95 V (i.e. with 170 mV overpotential) over 8 hrs is measured to be 0.1 ml. Correspondingly 1.86 C of charge is dissipated from the electrode (see figure below). Thus a FY of 75% is estimated for a CPE experiment performed with <200 mV overpotential. The low FY is likely due to solubility of the  $O_2$  produced in a degassed buffered solution.

Figure S14: CPE at 0.95 V vs NHE with Co-Ac-WOC on FTO.

