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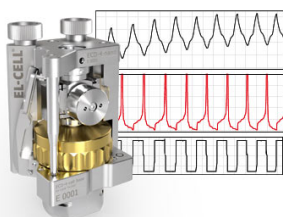
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## Increasing Chlorine Selectivity through Weakening of Oxygen Adsorbates at Surface in Cu Doped RuO<sub>2</sub> during Seawater Electrolysis

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During seawater electrolysis, both oxygen and chlorine evolve at anode and their selectivity can be modulated through variation of surface and electronic structure of the electrocatalyst. In this context, the selectivity toward chlorine evolution reaction (CER) during seawater electrolysis using electrodeposited Cu-doped RuO<sub>2</sub> with lower doping concentration (2%) has been found to be better than RuO<sub>2</sub>. Though Cu does not behave as an active site it reduces the binding energy of oxygen evolution reaction (OER) related intermediates (e.g. HO-, O-, HOO-) in neighboring Ru active sites and promotes both specific activity and selectivity of CER as suggested by both experimental and Density Functional Theory studies. However, due to aliovalent nature of Cu-dopant in RuO<sub>2</sub> host, phase segregation and surface enrichment of dopants occur with increase in dopant concentration which reduces the overall activity and selectivity toward CER. Furthermore, increase in Cu-dopant would lower surface oxygen vacancy formation energy and promotes additional lattice-oxygen-vacancy aided water dissociation pathway resulting in enhancement of selectivity of OER. The present work offers insight on catalyst design taking account of selectivity of chlorine and oxygen evolution during seawater electrolysis.

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The seawater electrolysis has gained much attention in recent years as it provides chemical fuel such as hydrogen and oxygen while also generating chlorine which is important for producing other valuable chemicals like pesticides and insecticides.<sup>1,2</sup> During electrolysis, Cl<sub>2</sub> and O<sub>2</sub> evolve at anode and their respective thermodynamic evolution potential is 1.36 V and 1.23 V, respectively, with respect to SHE.<sup>2,3</sup> However, Cl<sub>2</sub> co-evolves with O<sub>2</sub> arising from solvent water splitting. This necessitates designing of electrocatalysts selective to Cl<sub>2</sub> evolution reaction (CER) which is important for synthesizing chemical products out of seawater electrolysis. Generally, Ru-based electrocatalysts are used for seawater electrolysis.<sup>4–12</sup> In this regard, doping of aliovalent cations in RuO<sub>2</sub>, having valency lower than the host cation, promotes<sup>1</sup> bulk and surface vacancies which improve its electrical conductivity thereby lowering the resistance to charge transport through electrocatalyst<sup>13,14</sup> and<sup>2</sup> vacancies create steps and kinks on surface which may improve electrocatalytic activity.<sup>15</sup> Taking account of these positive effects of aliovalent dopants, Cu is chosen as dopant to RuO<sub>2</sub> as it can have maximum valency +2 with a maximum co-ordination of 4 and it would promote oxygen vacancies in RuO<sub>2</sub> crystalline structure. Also, Cu-doping would increase the number of d-electrons in the band-structure of RuO<sub>2</sub> as Cu have d<sup>9</sup> electronic configuration as opposed to d<sup>6</sup> configuration and expected to weaken binding strength with O<sub>2</sub> evolution reaction (OER) intermediates (-OH, -O, -OOH)<sup>16–18</sup> which is expected to retard OER kinetics.

In the present work, Cu-doped RuO<sub>2</sub> electrocatalyst has been made through electrodeposition technique and its selectivity toward CER investigated in a 0.5 M NaCl solution which is taken as a model solution for seawater. The amount of evolved Cl<sub>2</sub> and O<sub>2</sub> gas are measured through a combination of gas-chromatography and electrochemical techniques. It is found that the selectivity and specific activity of CER is at the maximum at a low doping concentration of Cu (2%). The specific activity of OER increases with dopant concentration of Cu before getting saturated. With increase of Cu concentration, there is high probability of surface segregation and Cu –

oxides formation. The increase of Cu-dopant concentration is accompanied by all-inclusive reduction in specific activity and selectivity of CER. However, aliovalent doping increases the electrochemical surface area (ECSA) through corrugation of surface which is promoted due to facile formation of oxygen vacancies.<sup>13,19,20</sup> Increase of dopant concentration reduces stability of doped RuO<sub>2</sub> due to surface and phase segregation of Cu-oxides as they are less stable than RuO<sub>2</sub> under reaction condition. To understand the governing mechanism aiding CER over OER, density functional theory (DFT) based simulations are performed. It suggests that though Cu is not an active site for CER, it reduces the binding energy of OER intermediates (e.g. HO-, O-, HOO-) in neighboring Ru active sites through a combination of ‘strain’ and charge transfer effects which promotes both specific activity and selectivity of CER. Increase in Cu-dopant lowers vacancy formation energy of surface oxygen and thus, promoting an additional lattice oxygen vacancy aided water dissociation pathway resulting in enhancement of selectivity of OER at higher concentration of doping.<sup>21</sup> We believe that present insight on catalyst design would help in achieving better selectivity and specific activity toward CER during seawater electrolysis.

### Results and Discussion

**Electrode preparation.**—Cu-doped RuO<sub>2</sub> electrocatalysts with different Cu concentration were being electrodeposited on a Ti-support by varying the Cu-precursor solution from 5 μM–0.1 M (Table I) through chronoamperometric method. Before starting of the electrodeposition process, Ti plate was scrubbed by emery paper, sonicated for 30 minutes in acetone, cured with oxalic acid at 100°C to make it free from any possible surface oxide layer from its surface and rinsed with DI water. The solution bath for electrodeposition process was prepared by mixing the precursor salts (RuCl<sub>3</sub>, xH<sub>2</sub>O and CuSO<sub>4</sub>.5H<sub>2</sub>O) in DI water followed by the addition of 1 M NaCl. The bath solution was stirred at room temperature, followed by 0.5 wt% boric acid addition and further stirring of 20 minutes. The well mixed solution of precursors was utilized for electrodeposition on the pretreated Ti-plate via a three-electrode setup assembly using

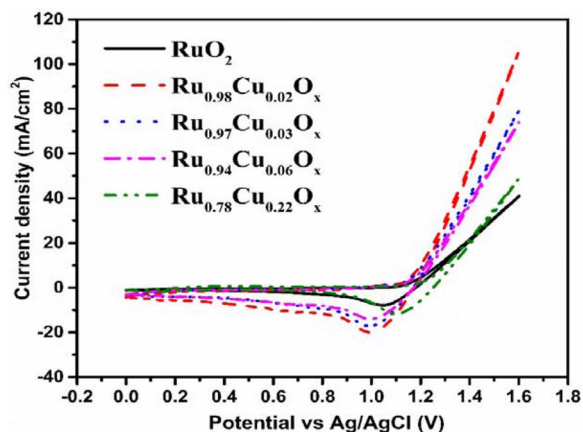
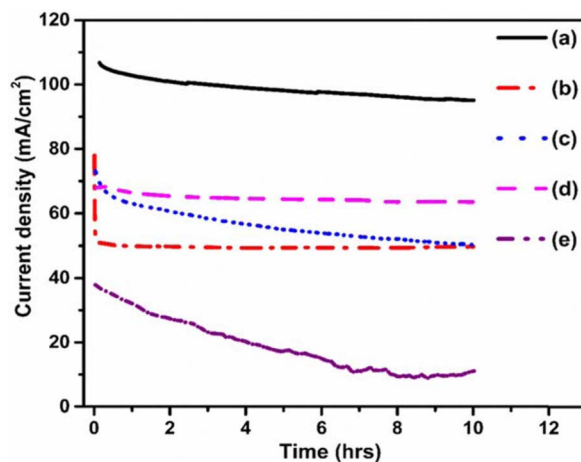
<sup>z</sup>E-mail: [rpala@iitk.ac.in](mailto:rpala@iitk.ac.in)

**Table I.** The concentration of Cu in the solution bath during electrodeposition to form RuO<sub>2</sub>, Cu doped RuO<sub>2</sub> and mixed RuCuO<sub>x</sub> on Ti-support.

S. No	Electrode	Cu-concentration in bath ( $\mu\text{M}$ )
1	RuO <sub>2</sub>	0
2	Ru <sub>0.98</sub> Cu <sub>0.02</sub> O <sub>x</sub>	5
3	Ru <sub>0.97</sub> Cu <sub>0.03</sub> O <sub>x</sub>	10
4	Ru <sub>0.94</sub> Cu <sub>0.06</sub> O <sub>x</sub>	50
5	Ru <sub>0.78</sub> Cu <sub>0.22</sub> O <sub>x</sub>	100

Pt as a counter electrode for 20 min. The compositions of Ru- and Cu-based precursor solution were varied by changing Cu-precursor concentration to get different composition of Cu- in the electrocatalysts. The electrodeposition is carried out in electrochemical hydrogen evolution zone ( $-0.8\text{ V}$  vs Ag/AgCl) which is known to roughen the electrode surface.<sup>13,22</sup> However, decreasing the electrodeposition potential further hampers nucleation and subsequent crystal growth of metal clusters on the substrate due to gas-bubbles arising out from hydrogen evolution reaction. Increasing the deposition potential from  $-0.8\text{ V}$  (vs Ag/AgCl) makes Ru deposition sporadic due to lower thermodynamic driving potential. After electrodeposition, the electrode samples are heated to oxides through annealing at  $550^\circ\text{C}$  for 5 hrs and subjected to detailed physico-electrochemical analysis.

**Electrocatalytic activity.**—Electrocatalytic activity and stability of electrodeposited Cu-doped RuO<sub>2</sub> have been analyzed through cyclic voltammetry (CV) (Figure 1) and chrono-amperometry in 0.5 M NaCl solution and compared with undoped RuO<sub>2</sub> electrocatalyst. The electrodes are used for 10 hrs during seawater electrolysis at a potential of  $2.01\text{ V}$  vs RHE<sup>23</sup> in 0.5 M NaCl solution to assess its stability. The activity and selectivity of the electrocatalysts toward CER are benchmarked at  $2.01\text{ V}$  vs RHE and summarized in Table II. The CER activity of Cu-doped RuO<sub>2</sub> electrocatalyst vis-à-vis geometric surface area (GSA) was found to be maximum at a doping concentration of 2%. However, the apparent activity vis-à-vis GSA is not a good measure of the performance of the electrocatalyst and the specific activity which considers of ECSA is calculated for this reason. It is found that ECSA is maximum for 2% Cu-doping concentration in RuO<sub>2</sub> (Table II). Also, the chlorine selectivity and specific activity of CER was found to be maximum at this concentration (Table II). The CER selectivity, specific activity of CER and ECSA decrease with increasing Cu-content in the electrodes. This may be correlated to the fact that with increase of Cu-content in electrodes, it would surface- and phase-segregate and as Cu or its oxides are poor electrocatalyst for CER themselves, causing decrease of CER selectivity and activity from the prepared electrode samples.

**Figure 1.** Cyclic voltammetry (CV) analysis of RuO<sub>2</sub> and different Cu concentration based RuO<sub>2</sub> in 0.5 M NaCl solution at 10 mV/s.**Figure 2.** Stability analysis of electrodes by chronoamperometric technique in 0.5 M NaCl solution at  $2.01\text{ V}$  vs RHE of (a) Ru<sub>0.98</sub>Cu<sub>0.02</sub>O<sub>x</sub> (b) Ru<sub>0.97</sub>Cu<sub>0.03</sub>O<sub>x</sub> (c) Ru<sub>0.94</sub>Cu<sub>0.06</sub>O<sub>x</sub> (d) Ru<sub>0.78</sub>Cu<sub>0.22</sub>O<sub>x</sub> (e) RuO<sub>2</sub>.

The doped oxide electrocatalysts are fairly stable under electrochemical oxidative condition under prolonged stability test conditions (Figure 2). In general, the corrosion of Cu is significant in low pH solutions, but becomes relatively sluggish at increased pH due to the formation of protective surface hydroxide thin film.<sup>24</sup> The addition of Cu provides significant stability to RuO<sub>2</sub> electrocatalyst and reduction of current density of  $\sim 10\%$  is found at a Cu-dopant concentration of 2% in RuO<sub>2</sub> whereas almost 75% reduction is found for undoped RuO<sub>2</sub> during stability test. The observed enhanced stability is probably because the dissolution pathway of RuO<sub>2</sub>  $\rightarrow$  RuO<sub>4</sub> involving adsorption of O<sup>-</sup> on the surface which is suppressed the presence of Cu as shown by our theoretical studies (Table III).

**Structural characterization.**—To further explore the effects of doping, structural characterizations were carried out. XRD analysis shows only peaks of rutile phase of RuO<sub>2</sub>, along with peaks of metallic Ru and Ti support up to Cu-concentration of 6% indicating successful doping (Figure 3e). However, the crystallinity of RuO<sub>2</sub> starts to reduce with increasing Cu-concentration though phase structure (crystallinity) of Ru-remains unaffected. This may be because oxygen vacancy increases with increasing dopant concentration, thereby reducing the crystallinity. The electrode having 22% of Cu shows additional peaks of CuO indicating phase segregation, which is a common phenomenon in high concentration of aliovalent doping.<sup>5,25</sup> Morphological analysis through SEM shows pin like small overgrowth upon film like structure (Figures 3a–3c). These pin like overgrowths might be providing increased roughness and higher surface area for electrocatalytic reactions. However, the films show cracks upon phase-segregation of CuO (Figure 3d). These cracking of films occur due to non-synchronized growth of Cu- and Ru-nucleation centers during electrodeposition and non-equivalent thermal expansion of Ru- and Cu-oxides during annealing.<sup>13</sup> Also, increase of dopant concentrations in RuO<sub>2</sub> causes higher number of oxygen vacancies which is also responsible for crack formation.

The chemical state and the surface elemental composition of the components are analyzed by XPS studies (Figure 4a). The XPS spectrum shows two peaks at 288 eV and 283.5 eV which are attributed to 3d<sub>3/2</sub> and 3d<sub>5/2</sub> of Ru (IV) peaks in Ru<sub>0.98</sub>Cu<sub>0.02</sub>O<sub>x</sub>. The peak corresponding to 2p<sub>3/2</sub> of Cu atom is detected at  $\sim 932.2\text{ eV}$  for metal and  $\sim 934\text{ eV}$  for oxide state (+2) respectively (Figure 4b). The metallic Cu is not detected during XRD indicating that there is very low concentration of metallic surface Cu atoms.

**Simulation studies and discussion.**—The CER selectivity of RuO<sub>2</sub> and Cu-doped RuO<sub>2</sub> were investigated using DFT in the VASP code. Since, RuO<sub>2</sub> (110) surface is having the lowest surface

**Table II. Comparison of the activity of electrodeposited RuO<sub>2</sub>, Cu doped RuO<sub>2</sub> and mixed Ru<sub>1-z</sub>Cu<sub>z</sub>O<sub>x</sub> on titanium support.**

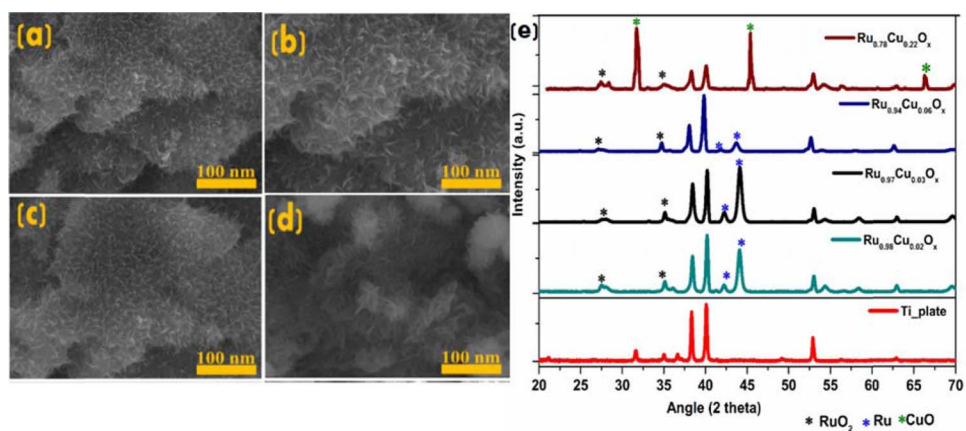
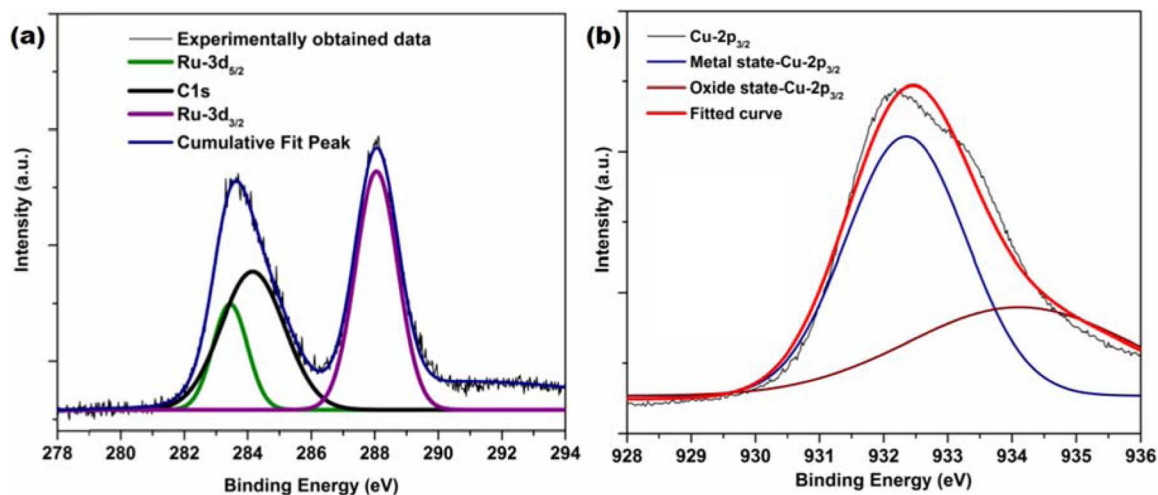
S. No	Electrodes	Current density of CER (mA/cm <sup>2</sup> ) at 2.01 V vs. RHE	Specific activity of CER (μA/cm <sup>2</sup> ) at 2.01 V vs. RHE	Chlorine selectivity	ECSA (cm <sup>2</sup> )
1	RuO <sub>2</sub>	7.63	20.2	0.39	378
2	Ru <sub>0.98</sub> Cu <sub>0.02</sub> O <sub>x</sub>	51.27	65.9	0.95	778
3	Ru <sub>0.97</sub> Cu <sub>0.03</sub> O <sub>x</sub>	35.26	61.7	0.86	571
4	Ru <sub>0.94</sub> Cu <sub>0.06</sub> O <sub>x</sub>	28.88	61.4	0.76	449
5	Ru <sub>0.78</sub> Cu <sub>0.22</sub> O <sub>x</sub>	12.98	31.7	0.59	410

**Table III. Binding energies of O\*, HO\*, ClO\* and Cl\* on Cu-doped RuO<sub>2</sub> (110) surface and pure RuO<sub>2</sub> (110) under electrochemically oxidative and acidic (pH = 0.0) condition.**

	ΔG <sub>OH</sub> (eV)	ΔG <sub>O</sub> (eV)	ΔG <sub>OOH</sub> (eV)	ΔG <sub>OCl</sub> (eV)	ΔG <sub>Cl</sub> (eV)
Pure RuO <sub>2</sub>	0.83	1.99	3.69	1.72	#
Cu-doped RuO <sub>2</sub> (cus)	1.89	4.23	4.15	^	1.86
Cu-doped RuO <sub>2</sub> (br)	1.08	2.06	3.61	^	1.41
Cu-doped RuO <sub>2</sub> (ss1)	0.73	1.86	3.64	1.76	#
Cu-doped RuO <sub>2</sub> (ss2)	0.91	2.09	3.82	1.69	#

^Formation of ClO\* structure is energetically unviable since at Cl\* would form at lower electrochemical potential.

#Formation of Cl\* structure is energetically unviable since HO\* and O\* formation would form at lower electrochemical potential.

**Figure 3.** SEM images of electrodeposited RuCuO<sub>x</sub> on Ti plate (a) Ru<sub>0.98</sub>Cu<sub>0.02</sub>O<sub>x</sub> (b) Ru<sub>0.97</sub>Cu<sub>0.03</sub>O<sub>x</sub> (c) Ru<sub>0.94</sub>Cu<sub>0.06</sub>O<sub>x</sub> and (d) Ru<sub>0.78</sub>Cu<sub>0.22</sub>O<sub>x</sub> (e) X-ray diffraction (XRD) pattern of different composition of electrodeposited Ru<sub>1-z</sub>Cu<sub>z</sub>O<sub>x</sub> on Ti support.**Figure 4.** X-ray photoelectron spectroscopy (XPS) spectra of (a) Ru zone and (b) Cu-zone of Ru<sub>0.98</sub>Cu<sub>0.02</sub>O<sub>x</sub>.

**Table IV. Theoretical overpotential ( $\eta^{\text{OER}}$ ) of OER and overpotential ( $\eta^{\text{CER}}$ ) of CER on undoped RuO<sub>2</sub> (110) and Cu-doped RuO<sub>2</sub> (110) surface. Potential determining step is indicated in brackets. ( $\eta^{\text{OER}} = 1.23$ -onset potential of OER,  $\eta^{\text{CER}} = 1.36$ -onset potential of CER, CET = coupled electron transfer).**

	$\eta^{\text{OER}}$ through CET pathway (eV)	$\eta^{\text{CER}}$ through CET pathway (eV)	$\eta^{\text{OER}}$ through -Ru <sub>br</sub> activation (eV)
Pure RuO <sub>2</sub>	0.48 (HOO*)	0.36 (ClO*)	1.61 (O <sub>2</sub> desorption)
Cu-doped RuO <sub>2</sub> (cus)	1.11 (O*)	0.50 (Cl*)	1.11 (O*)
Cu-doped RuO <sub>2</sub> (br)	0.32 (HOO*)	0.05 (Cl*)	0.32 (HOO*)
Cu-doped RuO <sub>2</sub> (ss1)	0.55 (HOO*)	0.40 (ClO*)	1.50(O <sub>2</sub> desorption)
Cu-doped RuO <sub>2</sub> (ss2)	0.50 (HOO*)	0.33 (ClO*)	1.48(O <sub>2</sub> desorption)

energy among its low-index surfaces, the effect of electrocatalysis upon Cu-doping in this surface is considered. During electrodeposition Cu occupy surface and sub-surface sites of RuO<sub>2</sub> (110) surfaces, hence effect of all the dopant position is considered. It is found that Cu gets doped preferentially to 5 co-ordinated '-cus' position than to any other 6 co-ordinated position of Ru in RuO<sub>2</sub> as Cu makes 4 co-ordinated oxides preferentially.

Binding energies of HO\*, O\*, HOO\*, Cl\* and ClO\* adsorbates on RuO<sub>2</sub> (110) surface are computed (\* = cus site of RuO<sub>2</sub>). It is found that the theoretical overpotentials for OER and CER are 0.48 eV and 0.13 eV respectively for undoped RuO<sub>2</sub> which corroborates well with literature.<sup>26,27</sup> The rate determining step is found to -OOH and -OCl formation for OER and CER respectively. However, upon Cu doping, the binding energy for -O adsorbate drastically weakens irrespective of dopant position (becomes more +ve) (Table III). The binding energy -O becomes so unfavorable that -Cl and -OH coverage is favored instead of -O coverage over the electrocatalyst when Cu is doped at the surface. Even when Cu occupies subsurface position, the overpotential toward OER is higher than pure RuO<sub>2</sub> (Table IV). We hypothesize that the weakening of oxygen intermediates (HO\*, O\*, HOO\*) over doped RuO<sub>2</sub> (110) surface is due to increase of d-electrons in the system and in sync with previous studies.<sup>18</sup>

In doped RuO<sub>2</sub>, Cu<sub>cus</sub> sites do not promote neither OER nor CER as they bind weakly both OER and CER intermediates. However, 'charge transfer' and 'strain effect' on neighboring Ru<sub>cus</sub> sites affects their binding characteristics. The 'charge transfer' between Ru and Cu atoms is demonstrated by Bader studies. Since Ru is more electronegative than Cu, the electron density over Ru atom increases by 0.04 e- in doped oxides in comparison to undoped oxides. This makes oxidation of Ru (IV) to a higher oxidation state energetically more intensive, thus binding of OER intermediates difficult making the OER process unfavorable. However, the binding energy of ClO- or Cl- gets weakly affected due to Cu-doping (Table III). In configurations of Cu-doped RuO<sub>2</sub> comprising Cu at either -br or ss2 site, the binding of CER intermediates to Ru<sub>cus</sub> sites become energetically more favorable, which lowers theoretical  $\eta^{\text{CER}}$  by 0.31 eV and 0.03 eV respectively when compared with pure RuO<sub>2</sub> (Table IV). This is demonstrated experimentally in almost three times enhancement of specific activity of CER of Cu-doped RuO<sub>2</sub> in comparison to undoped RuO<sub>2</sub>.

The endothermic barrier of forming oxygen vacancy is reduced by as much as 1.54 eV due to -br doping of Cu in RuO<sub>2</sub>.<sup>28</sup> In these cases, OER is additionally promoted by water dissociation pathway aided by oxygen vacancies at -br sites<sup>4,21</sup> followed by Ru<sub>br</sub> also acting as an active sites<sup>29</sup> (Table IV). In undoped RuO<sub>2</sub>, the desorption of O<sub>2</sub> from a surface structure of HOO\* requires a high overpotential ( $\eta^{\text{OER}} = 1.61$  eV) making it less favored pathway. Occupation of Cu at -br position reduces the overpotential of OER ( $\eta^{\text{OER}} = 0.32$  eV) making -br also an active site. However, adsorption of -OCl and -Cl on Cu-doped -br site is not favored energetically. For this reason, there may be a reduction of CER has been observed experimentally.

## Conclusions

In present study, selectivity and specific CER activity has been increased through small aliovalent doping of Cu (2%) through facile electrodeposition process. Though Cu does not act as an active site

for CER, it modulates Ru active sites through 'strain' and 'charge-transfer' effect in such a way that binding energies of OER intermediates get reduced (more +ve) and CER intermediates are favored (more -ve) and thereby reducing theoretical CER overpotential. However, increase in doping concentration entails occupation of active sites by Cu atoms thus lowering of electrochemical activity. Additionally, the endothermic barrier of formation of surface oxygen vacancy get reduced thus promoting an additional vacancy promoted water dissociation pathway which increases the selectivity of OER and lowers the selectivity of CER. The present study offers new insight on aliovalent Cu doped RuO<sub>2</sub> electrocatalysts for seawater electrolysis in neutral medium.

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