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## **Co-catalysis: Role of Organic Cations in Oxygen Evolution Reaction on Oxide Electrodes**

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# Co-catalysis: Role of Organic Cations in Oxygen Evolution Reaction on Oxide Electrodes

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ABSTRACT Co-catalysis is promising approach towards enhancing activity of heterogeneous and homogeneous electrocatalysts. We report such synergic catalysis involving organic xanthylium-based catalyst, Xan<sup>2+</sup>, and oxides formed on the electrode surface. The oxygen evolution reaction (OER) was observed on working electrodes such as gold, platinum, glassy carbon, and boron-doped diamond, while some electrodes (titanium and fluorine-doped tin oxide) exhibited no OER activity. Based on experimental data supported by previously reported calculations, we propose a mechanism in which oxidized Xan<sup>2+</sup> activates electrode surface

towards the rate-determining O-O bond formation. In light of our findings, efficient OER electrocatalysis can be achieved using materials that strongly bind oxygen species and electron-deficient organic cations. This work has implications for energy storage systems that utilize OER.

The performance of heterogeneous electrocatalysts can be modulated using molecular cocatalysts to lower the overpotential or to improve the product selectivity.<sup>1-13</sup> For example, electrochemical reduction of carbon dioxide on metal electrodes produces carbon monoxide with high selectivity if imidazolium cations are used as co-catalysts,<sup>1-4</sup> while the formation of methanol is favored if pyridinium ions are employed.<sup>5-9</sup> Ongoing studies provide crucial insights into the mechanism of these co-catalysts,<sup>1-9</sup> but general consensus is yet to be achieved. The electrocatalytic OER can also be affected by organic co-catalysts.<sup>10-13</sup> Our group has shown that flavinium and acridinium cations (Et-Fl<sup>+</sup> and Acr<sup>+</sup>, Scheme1)<sup>11,12</sup> both exhibit electrodedependent behavior, but while Et-Fl<sup>+</sup> significantly accelerates OER,<sup>11</sup> Acr<sup>+</sup> inhibit electrocatalysis. Based on spectroelectrochemical studies and observed electrode dependence, it was hypothesized that hydroxylated flavin (Et-FIOH) interacts with the oxides formed on the electrode surface. On the other hand, Acr<sup>+</sup> also forms hydroxylated analog (AcrOH) but with a lower thermodynamic driving force (higher pseudobase pKa value, the term "pseudobase" is used in this manuscript to describe hydroxylated iminium or oxonium cations) than Et-Fl<sup>+</sup>. It is possible that inhibition of OER by Acr<sup>+</sup> due to the lower electrophilic character of Acr<sup>+, 12</sup> More recently. Bachmann and co-workers observed OER catalysis by pyridinium ions (MePy<sup>+</sup>,

MePyz<sup>+</sup> and MePym<sup>+</sup>, Scheme 1) and found that the catalytic efficiency directly correlates with the electrophilic character of the iminium ion (the best behavior was observed with MePy<sup>+</sup>).<sup>13</sup>



Scheme 1. Structure of organic cations utilized in electrocatalytic OER studies. The pseudobase  $pK_a$  for each compound are listed under the structures (Et-Fl<sup>+</sup>,<sup>14</sup> Acr<sup>+</sup>,<sup>12</sup> Xan<sup>2+</sup>,<sup>15</sup> MePy<sup>+</sup>,<sup>16</sup> MePym<sup>+</sup>, MePyz<sup>+17</sup>).

Considering that the electrophilic nature of iminium cations appears to play a crucial role in cocatalysis, we extended our investigation to an electron-deficient xanthylium cation  $Xan^{2+}$ (Scheme 1). Generally, xanthylium cations exhibit low pseudobase  $pK_{a}$ ,<sup>15</sup> which reflects their Lewis acidity. The dimer  $Xan^{2+}$  displays even higher electron-deficiency due to its dicationic nature. It is shown here that  $Xan^{2+}$  enhance electrocatalytic OER and that the process is cocatalyzed by the oxides formed on the electrode surface. By analyzing a series of electrode materials, we identify key parameters that lead to accelerated OER. These findings provide crucial design parameters for future synergic OER co-catalysts.

The cyclic voltammogram (CV) of  $Xan^{2+}$  in acetonitrile (Figure 1A) indicates that the electrocatalytic process occur with the onset potential of 2 V vs ferrocene/ferrocenium (Fc/Fc<sup>+</sup>), as indicated by an increase in the current density relative to the baseline (red vs black curve). To confirm that the process involves catalysis rather than chemically irreversible anodic oxidation of  $Xan^{2+}$ , the  $Xan^{2+}/Xan^{2\bullet}$  quasi-reversible reduction<sup>18</sup> at -0.26 V vs Fc/Fc<sup>+</sup> was used as a marker. The current density at -0.26 V obtained during the cathodic scan (blue curve) matches in intensity with the current density at the same potential recorded after initial anodic oxidation (red curve). The full recovery of the cathodic peak is consistent with the catalytic process, since chemically irreversible anodic oxidation would cause a decrease in the current.<sup>11</sup> Addition of water to the acetonitrile solution caused an increase in the background-subtracted current density at 2.39 V (inset of Figure 1A and Figure S1), confirming that the catalysis involves oxidation of water. Controlled potential electrolysis experiments in acetonitrile/water mixture show that the amount of oxygen evolved significantly increases in the presence of  $Xan^{2+}$  (Figure 1B), further supporting that OER on Pt working electrode is co-catalyzed by  $Xan^{2+}$ .



**Figure 1.** A) CVs of 1.5 mM Xan<sup>2+</sup> in acetonitrile using 0.1 M tetrabutylammonium perchlorate (TBAP) as electrolyte. Scan direction: red and black curve +0.19 V $\rightarrow$  +2.39 V $\rightarrow$  -0.89 V $\rightarrow$  +0.19 V; blue curve, +0.19 V $\rightarrow$  -0.89 V $\rightarrow$  +0.19 V. The black line represents the background current. Working electrode: Pt; dashed lines show the equilibrium potential for OER (for detailed calculations see Supporting Information, SI) and the observed potential for catalytic water oxidation by Et-Fl<sup>+</sup>;<sup>11</sup> inset figure shows the percent current increase at 2.39 V with the concentration of pH 0.5 water (I<sub>w</sub> and I<sub>nw</sub> represents current in the presence and absence of water respectfully); B) Oxygen evolution during the electrolysis of 1 mM Xan<sup>2+</sup> in 0.1 M phosphate solution at pH= 0.5 (red) (30% faradaic efficiency), the black line represent the amount of oxygen evolved in the absence of Xan<sup>2+</sup> (86 % faradic efficiency); applied potential: +2 V vs

Fc/Fc<sup>+</sup>. Working electrode: Pt; C) CVs of 1.5 mM DPE (green), Mono<sup>+</sup> (red), and Xan<sup>2+</sup> (blue) in 0.1 M TBAP/acetonitrile; black line shows the background scan involving only electrolyte solution; Pt as working electrode; D) Spin density of Xan<sup>3+</sup> calculated at the uB3LYP 6-311g(d) level of theory.

Recent estimate of the standard reduction potential for  $O_2/H_2O$  couple in acetonitrile<sup>19</sup> allowed us to evaluate the overpotential associated with Xan<sup>2+</sup> co-catalysis. The equilibrium potential for  $O_2/H_2O$  couple under our experimental conditions was evaluated to be 1.01 V vs Fc/Fc<sup>+</sup> (derivation details are summarized in Section 1, SI), while the onset of the catalytic peak in the presence of Xan<sup>2+</sup> appears at 2 V. This almost 1 V overpotential is significantly larger than that observed with N-containing heteroaromatic cations. For example, the electrocatalysis by Et-Fl<sup>+</sup> occurs at 1.27 V vs Fc/Fc<sup>+</sup>,<sup>11</sup> at an overpotential of only 0.26 V. The differences in overpotentials reflect the fact that, due to lower electronegativity of the nitrogen, N-containing heteroaromatic cations oxidize at less positive potentials than O-containing derivatives (for example, oxidation potential of phenol is 1.04 V, while the oxidation potential of aniline is 0.74 V.<sup>20</sup>

To identify the oxidation site that is responsible for catalysis, the CV of Xan<sup>2+</sup> was compared to individual fragment molecules, namely monomeric xanthylium cation (Mono<sup>+</sup>, red line Figure 1C) and diphenyl ether (DPE, green line, Figure 1C). While Mono<sup>+</sup> undergoes an irreversible oxidation with anodic peak current at a 2.35 V vs Fc/Fc<sup>+</sup>, the oxidation of DPE occurs at a significantly lower potential of 1.45 V. The lower potential of DPE suggests that the oxidation of Xan<sup>2+</sup> at 2 V involves the removal of an electron from the diphenyl ether linker. These findings are further supported by the spin density distribution for one-electron oxidized Xan<sup>3+</sup> radical showing high spin density on carbon atoms localized on diphenyl ether moiety (Figure 1D). Interestingly, even though the oxidation site involves diphenyl ether, anodic behaviors of DPE

and  $Xan^{2+}$  are considerably different. The oxidation of DPE is known to trigger the polymerization reaction, forming insoluble poly(diphenyl-ether) that deposits on the electrode surface.<sup>21</sup> This process can be readily visualized in multiple-scan voltammograms, which exhibit a current decrease in each consecutive scan, due to polymer deposition (Figure S2A). In contrast, multiple scans of  $Xan^{2+}$  do not display any decrease in the current (Figure S2B), consistent with OER catalysis observed in Figure 1.

In agreement with our previous studies involving iminium ions Et-Fl<sup>+</sup> and Acr<sup>+</sup> (Scheme 1),<sup>11-12</sup> electrocatalytic behavior of Xan<sup>2+</sup> showed strong dependence on the working electrode material. The anodic behavior was studied on six different working electrodes that exhibit different abilities to oxidize water to oxygen: platinum, gold, titanium, fluorine-doped tin oxide (FTO), glassy carbon (GC), and boron-doped diamond (BDD). While CVs on all electrodes displayed signature reduction peak of Xan<sup>2+</sup> at -0.26 V vs Fc/Fc<sup>+</sup> (Figures S3 and S4, SI), the catalytic peak at 2 V was observed only on some electrodes (Pt, Au, GC and BDD). This effect is clearly illustrated in Figures 3A and B, which show a strong catalytic current when Au electrode is used and the complete absence of the current with FTO. Additional evidence that the electrode surface plays a key role in OER comes from our experiments involving chemical water oxidation in the presence of sacrificial electron acceptor (Figure S5). In specific, water oxidation by persulfate ions was studied in the presence and absence of Xan<sup>2+</sup>. Persulfate facilitates oxidation in two possible ways: (1) as persulfate ion, where the standard reduction potential for  $S_2O_8^{2-} + 2e^- \rightarrow$  $2SO_4^{2-}$  is +2.01 V vs NHE;<sup>22</sup> (2) as sulfate radical anion formed thermally from persulfate, where the potential for  $SO_4^- + e^- \rightarrow SO_4^{2-}$  is +2.43 V vs NHE.<sup>23</sup> Our experiments were performed at elevated temperature to utilize higher oxidative power of persulfate radical anion. Even though the oxidation of Xan<sup>2+</sup> occurred (monitored by UV/Vis absorption, Figure S6), the amount of

oxygen evolved in the presence of  $Xan^{2+}$  was lower than in its presence (Figure S5), indicating that  $Xan^{2+}$  by itself cannot catalyze oxidation of water to oxygen.



**Figure 2.** CVs of 1.5 mM Xan<sup>2+</sup> in 0.1 M tetrabutylammonium hexafluorophosphate/acetonitrile on A) gold, and B) FTO working electrode. Black lines represent background currents. C) Dependence of catalytic current on  $\varepsilon$ . The y-axis plots experimentally obtained catalytic current, represented as  $\frac{I_{cat}-I_b}{I_d}$ , where I<sub>cat</sub> is catalytic current in the presence of Xan<sup>2+</sup>, I<sub>b</sub> is the baseline current at the same potential, and I<sub>d</sub> is current associated with the Xan<sup>2+</sup> reduction peak at -0.26 V.

Given the observed dependence of the electrocatalytic current on the working electrode, we postulate that surface oxides play an active role in the chemical transformations occurring during OER. Thus, we turn our attention to heterogeneous mechanisms observed on oxide electrodes, where OER is often modeled computationally using adsorbed \*OH, \*O and \*OOH intermediates, as presented in Scheme 2. Gibbs free energies for the formation of surface-adsorbed oxygen species are expressed as:

 $H_2O + * \rightarrow *OH + e^- + H^+ \Delta G_{H2O/*OH}$ 

 $*OH \rightarrow *O + e^- + H^+ \Delta G_{*OH/*O}$ 

These energies were obtained previously using density functional theory calculations, <sup>24-26</sup> and the values for oxides used in this study are tabulated in Table S1 (details in Section 3).

Calculated  $\Delta G_{H2O/*OH}$  values indicate that \*OH species are likely present on all working electrodes at the potential at which the electrocatalysis is observed. In the case of \*O species, the potential at which these oxides are expected to form ( $\epsilon$ ) is relatively low for Au, Pt and C surfaces, while it is significantly higher for Ti and Sn oxides. Even though quantitative analysis is not possible due to differences in the computational methods and due to differences between experimental conditions and computational models, the qualitative agreement seems to exist between the observed current and the calculated  $\epsilon$  values (Figure 2C). The catalytic current appears on electrode surfaces that efficiently form \*O species at the applied potential (Au, Pt, C), and the amount of current seems to correlate with the calculated  $\epsilon$  value. In contrast, no catalysis was observed on Sn and Ti oxide surfaces, where the Gibbs free energy for \*O is exceptionally high.

The correlation presented in Figure 2C strongly suggests that electrocatalysis by  $Xan^{2+}$  is initiated by its binding to \*O species on electrode surface. The question that remains unanswered is how this binding affects electrocatalysis. Nørskov has shown that the potential-determining step for OER depends on how strongly the electrode binds oxygen species.<sup>24</sup> If \*O is bound too strongly to the surface, as is the case for Pt,<sup>25</sup> Au<sup>25</sup> and C<sup>26</sup> electrodes, then the potential determining step is the \*OOH formation. Thus, it is very likely that  $Xan^{2+}$  and other cations presented in Scheme 1 affect this step either by lowering the kinetic barrier for \*O  $\rightarrow$  \*OOH conversion or by fully circumventing the formation of \*OOH species (for example, by forming the \*OOR intermediate, where R is the molecular co-catalyst). Both of these mechanisms are possible and were proposed previously.<sup>11-12</sup> However, our recent studies indicate that the formation of \*OOR species is a less likely mechanism, since the formation of RO species is a

proton-coupled process that is not feasible for all cations presented in Scheme 1.<sup>27-28</sup> It is more likely that the co-catalysis involves the lowering of kinetic barrier for  $*O \rightarrow *OOH$  conversion, as presented in Scheme 2. According to this mechanism, an ether-like  $*OR^{3+}$  intermediate makes an oxygen center highly electron-deficient and activates it towards nucleophilic attack by a water molecule to form the critical O-O bond.



Scheme 2. Proposed mechanism for OER by co-catalysis involving electrode surface oxides and electron-deficient molecular catalysts presented in Scheme 1. Inset is showing proposed structure of  $*OR^{3+}$  formed between electrode oxides and Xan<sup>2+</sup>.

Based on the mechanism proposed in Scheme 2, efficient co-catalysis can be achieved with the working electrode made of materials that strongly bind \*O species and with small-molecule cocatalysts that are electron-deficient and behave as strong Lewis acids upon one-electron oxidation. While the oxidation potential of Xan<sup>2+</sup> is significantly higher than the thermodynamic potential for OER, the potential can be lowered using iminium-based cations, such as flavinium or pyridinium systems studied previously.<sup>11, 13</sup> The list of oxides that strongly bind \*O species is available through computational<sup>24-25</sup> and experimental<sup>29</sup> studies. In synergy with Lewis acid co-catalysts presented in Scheme 2, these oxides are expected to show accelerated OER activity. It

is interesting that carbon-based electrodes also bind \*O strongly, thus opening the possibility of fully metal-free co-catalysis, potentially utilizing graphene-based materials with OER activity.<sup>30</sup>

# ASSOCIATED CONTENT

**Supporting Information**. The Supporting Information is available free of charge on the ACS Publications website. Experimental methods, calculated  $Xan^{3+}$  coordinates, details on equilibrium potential,  $\Delta G$ , and  $\epsilon$  derivation, Figures S1-S6. (PDF)

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#### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval

to the final version of the manuscript.

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