Mechanistic Investigation of Electrochemical Hydrogen Evolution from Water Catalyzed by a Co-NHC Complex

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Hydrogen production based on water splitting using solar energy has attracted much attention. Our laboratory previously reported that an N-heterocyclic carbene cobalt complex, **Co-NHC1**, promotes photochemical hydrogen evolution from water with low driving force.[1,2] In this study, mechanistic studies on hydrogen evolution reaction (HER) by **Co-NHC1** were carried out through the advanced electrochemical analyses.

The concentration dependence of the phosphate buffer solution was evaluated by conducting linear sweep voltammogram (LSV) measurement at pH = 7 (Figure 1). As a result, it was found that one $H_2PO_4^-$ molecule is involved as a proton mediator during the PCET-based (proton-coupled electron transfer) reduction process towards Co(II), which is considered as the rate-limiting step. Importantly, the turnover frequency of HER catalyzed by **Co-NHC1** was estimated to be 25,000,000 s^{-1}, showing that **Co-NHC1** has exceptionally high catalytic activity of HER. Next, kinetic isotope effect (KIE) was evaluated, where the KIE was estimated to be 13.7. It strongly indicates that the Co(III)-H formation process proceeds via the CPET (concerted proton-electron transfer) process. More importantly, a linear correlation was observed between the maximum catalytic current ($i_{cat,max}$) and the concentration of **Co-NHC1** (Figure 2), where $i_{cat,max}$ values were determined from the plateau-shaped currents obtained by increasing the scan rate. Therefore, it can be concluded that the HER catalyzed by **Co-NHC1** proceeds via a unimolecular pathway.

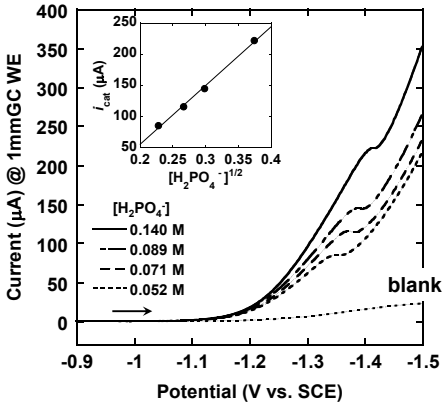

Figure 1. LSVs for the aqueous phosphate buffer solutions (pH = 7; [$H_2PO_4^-$] =0.052-0.14 M) of 18 μM **Co-NHC1** (WE: GC, CE: GC, RE: SCE, Scan rate: 0.1 V/s).

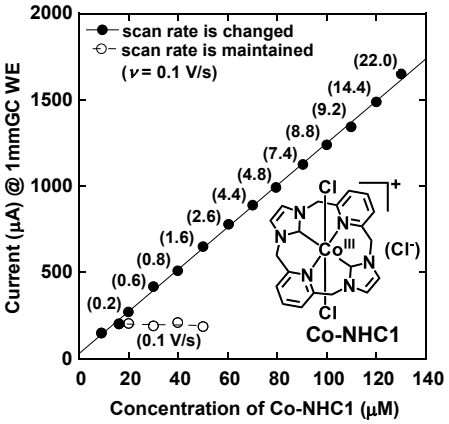

Figure 2. Concentration dependence of $i_{cat,max}$ values for the LSVs using aqueous phosphate buffer solutions (0.4 M, pH = 7.0) of **Co-NHC1** (10-130 μM).

1) K. Kawano, K. Yamauchi, K. Sakai, *Chem. Commun*. **2014**, *50*, 9872. 2) K. Yatsuzuka, K. Yamauchi, K. Kawano, H. Ozawa, K. Sakai, *Sustainable Energy Fuels* **2021**, *5*, 740.