ELECTROCATALYTIC WATER OXIDATION BY COBALT-CARBONATE

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Water oxidation ($2H_2O—>O_2+4H^++4e^-$) is a key step in artificial photosynthesis. It has significant importance in biological processes, solar energy conversion and water electrolysis. Herein we present the homogeneous electro-catalytic water oxidation by cobalt-carbonate (Co-C) system. It is shown that cobalt-carbonate acts as an efficient water oxidation catalyst with onset potential of 1.22 V and peak/plateau of 1.36 V vs. Ag/AgCl with a current density of 10.5 mA cm^{-2} at an overpotential of 680 mV. Before catalysis, there appears a Co$^{III/II}$ peak with Epa at around 0.72 V. This peak is electrochemically irreversible and dependent on bicarbonate, carbonate, and metal salt concentrations as well as pH. It follows a proton-coupled electron transfer (PCET) where the CoII is stabilized by mono-dentate bicarbonate and water whereas the CoIII is coordinated to bidentate carbonate ligands. The peak shifts cathodically with increasing metal salt concentration, which means that a dimer is formed after oxidation. The catalyst further undergoes oxidation to form a CoIV=O species which then forms peroxo/percarbonate intermediates followed by the release of oxygen and goes back to its initial state. The catalytic current depends linearly with the metal salt concentration. The Tafel slope is calculated to be 195 mV dec^{-1}. After chronoamperometry at 1.3 V for 3.5 hours, a green solution is formed with a green deposit on the electrode surface. From the absorption spectra (peak at 258 nm), the green compound is found to be $Na_3[CoIII(CO_3)_3]$. The same peak is also observed after pulse radiolysis of CoSO4 in NaHCO3. The anodic peak current (id) of CoIII/II peak follows the Randles-Sevcik equation and thus the process is homogeneous and the rate constant (kcat) of catalysis is 100.5 s^{-1}. The rate constant (k0) of the electron transfer for the Co$^{III/II}$ peak is 0.85 x 10-3 cm s^{-1}.

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