Oxygen reduction at sub-monolayer of self-assembled thiols at gold electrodes: Effects of the extent of surface coverage on the reversibility of the reaction

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Introduction– The oxygen reduction reaction (orr) is a reaction of prime importance due to its vital role in energy conversion systems like fuel cell and metal-air batteries. This reaction proceeds irreversible at bare gold electrodes in alkaline media, while it's totally hindered at gold electrodes modified with a compact structure (i.e., complete monolayer) of cysteine (CYST) over its surface (SAM/Au).

Here, we demonstrate the effects of the surface coverage of an electrochemically inactive thiol compound (i.e., cysteine) assembled at gold electrode, towards the reversibility of the oxygen reduction reaction.

Experimental– The partial reductive desorption of the compact CYST monolayer was achieved by controlling the potential of the Cyst/Au electrode in N_2-saturated 0.5 M KOH (–300 to –800 mV (vs. Ag/AgCl) for two cycles at 50 mV s^{-1}, leading to the formation of a sub-monolayer coverage of CYST over the Au electrode surface (sub-SAM/Au).

Results and discussions- Fig. 1 shows the oxygen reduction reaction (orr) at gold electrodes with different surface coverage of CYST (Γ_{CYST}) in O_2-saturated 0.5 M KOH. This figure shows that the orr is completely retarded at the SAM/Au electrode (curve b). While a considerable enhancement of the reversibility of the orr was achieved at a sub-SAM/Au electrode having a surface coverage of 5.26×10^{-10} mol cm^{-2} (curve c). This electrode exhibits a quasi-reversible 2-electron reduction of O_2 (to HO_2^-). The employed potential range in the reductive desorption experiment led to the desorption of the CYST molecules that are loosely bounded to the smooth domains of the Au surface. While the strongly bounded CYST molecules retained at the rough domains of the Au surface. This leads to the inhibition of the disproportionation reaction of the produced HO_2^- at the sub-SAM/Au electrode (i.e., $HO_2^- = OH^- + ½\ O_2$), whereas this reaction is catalyzed at the rough domains of the bare Au surface, resulting in the excessive current supported by the bare Au electrode more than that supported by the sub-SAM/Au electrode. At the sub-SAM/Au electrode, and in the cathodic potential scan, the 2-electron reduction of O_2 proceeds at the bare fraction of the Au surface (i.e., uncovered with CYST). The ratio of the anodic current to the cathodic one is close to unity. The peak separation (ΔE_p) between the cathodic and anodic peak potentials (E_p^c, E_p^a) is about 60 mV, indicating that O_2 reduction is a quasi-reversible process at this electrode in alkaline medium. The formal potential ($E^{o'}$) of this reaction is found to equal –150 mV vs. Ag/AgCl/KCl(sat).

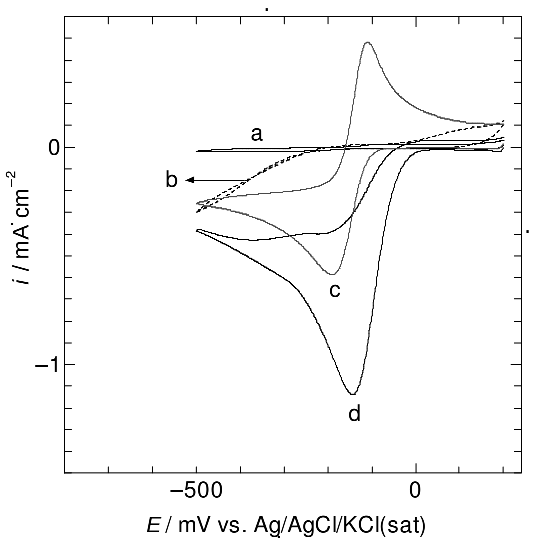

Fig. 1: CV response of (a, b) SAM/Au (Γ_{CYST} = 15.54×10^{-10} mol cm^{-2}), (c) sub-SAM/Au (Γ_{CYST} = 5.26×10^{-10} mol cm^{-2}) and (d) bare Au electrodes in (a) N_2-saturated and (b-d) O_2-saturated 0.5 M KOH. At a potential scan rate of 50 mV s^{-1}, ϕ = 1.6 mm.