Electronic Supplementary Information

Activating Ag by Even More Inert Au: Peculiar Effect on Electrocatalysis toward Oxygen Reduction in Alkaline Media

Cuixia Yang, Bing Huang, Li Xiao[*], Zhandong Ren, Zilong Liu, Juntao Lu, Lin Zhuang[*]

College of Chemistry and Molecular Sciences, Hubei Key Lab of Electrochemical Power Sources, Wuhan University, Wuhan 430072, China

chem.lily@whu.edu.cn, lzhuang@whu.edu.cn

I.   **Table S1**

II. **Computational detail**

III. **Experimental detail**

I. Table S1   Theoretical screening for stable Ag/M surface exhibiting greater oxygen affinity than usual Ag surface.

surface[a]	AE_O / eV[b]
Ag(111)	-0.27
Au(111)	0.03
Ag/Au(111)	-0.39
Au/Ag(111)	0.14
Ag/Cu(111)	0.23
Ag/Ir(111)	-0.08
Ag/Pd(111)	0.04
Ag/Pt(111)	0.07
Ag/Rh(111)	-0.02
Ag/Os(0001)	-0.15
Ag/Ru(0001)	-0.06

[a] Early transition metal surfaces are not considered here because the lattice sizes between Ag and the substrate are highly mismatched and early transition metal surfaces are practically not stable under electrochemical conditions. Also, Fe, Co and Ni surfaces turned out not to be compatible with Ag covering, the resulting Ag/M surface is not stable, probably because of the mismatch in lattice size.

[b] $AE_O = E(O/M) – E(M) – 1/2E(O_2)$, such that the negative value indicates the dissociation of O_2 on the studied surface being thermodynamically spontaneous, whereas the positive means the opposite.

II. Computational detail

DFT calculations were performed using the Vienna Atomic Simulation Package (VASP, version 5.3) within a RPBE generalized gradient approximation (GGA) to the exchange and correlation functional. A projected augmented wave (PAW) basis along with a plane-wave kinetic energy cutoff of 408 eV was used throughout. For the calculations of surface and chemisorption systems, a p(2×2) surface unit cell (corresponding to 1/4 coverage) was used to construct a six-layer metal slab and repeated in super cell geometry with successive slabs separated by a vacuum region equivalent to four metal layers, and the Brillouin zone was sampled using a 6×6×1 Monkhorst-Pack mesh. During the geometry optimization, the adsorbate layer and the top three layers of the slab were allowed to relax. The energies were converged to 1 meV per atom and ionic relaxations were allowed until the absolute value of force on each atom was below 0.02 eV/A.

III. Experimental detail

Preparation of Au and Ag RDEs. Various types of Au electrodes have been tested in this work, including commercial Au RDE (PINE Co.) and homemade ones prepared by sputtering and electrodeposition. Results produced by all these Au electrodes are essentially the same. In order to be comparable to the Ag RDE, which can only be prepared in our lab by electrodeposition, we reported in this paper the results of Au electrode prepared by electrodeposition.

A glassy carbon (GC) RDE (4.57 mm in diameter) was used as the substrate, and the deposition was carried out at a rotation rate of 1600 rpm in a deaerated KCl solution (0.1 M) containing 5×10^{-5} M $HAuCl_4$ or in a deaerated KNO_3 solution (0.1M) containing 5×10^{-5} M $AgNO_3$, respectively. A sheet of carbon paper was used as the counter electrode. For depositing Au, a Ag/AgCl (0.1M KCl) served as the reference electrode; while for depositing Ag, a Ag wire was used as the pseudo reference electrode. The electrode potential was fixed at -0.5 V (vs. Ag/AgCl) for Au deposition and -0.3 V (vs. Ag) for Ag deposition, where the reduction processes were both under diffusion control. In order to prepare Au and Ag electrodes with close electrochemical surface area, 1000s and 350s were chosen as the deposition time for Au and Ag, respectively.

Pb UPD. After electrochemical deposition, the Au or Ag RDE was rinsed with ultrapure water repeatedly prior to the following test. Pb UPD was carried out in a deaerated 1 M KOH solution containing 1×10^{-3} M $Pb(NO_3)_2$. For every experiment, a new sheet of carbon paper was served as the counter electrode in order to exclude any possible metal contamination introduced from the previous experiments. The reference electrode was a reversible hydrogen electrode (RHE) in the same electrolyte. The electrode potential was swept between 0.786 V and 0.236 V (vs. RHE). The negative sweep corresponds to the Pb UPD process, and the positive sweep is the subsequent stripping process.

Preparation of Au@Ag RDE. The Pb covered Au (Pb/Au) electrode was obtained by ending the potential sweep at 0.236 V (vs. RHE) in the above Pb UPD process. After repeatedly rinsing with ultrapure water, the Pb/Au electrode was rotated in 1×10^{-3} M AgNO$_3$ solution for a controlled period of time (up to 200s) for Ag displacement. Different displaced time can results in different Ag coverage, whose Pb UPD behavior will be different from that on Au or Ag electrodes, as illustrated in Fig. 1.

Electrochemical tests. All electrochemical experiments were performed in a conventional three-electrode cell at room temperature. The potentiostat was a CHI-700D. All reagents were of GR grade and solutions were prepared using ultrapure water (18 MΩ·cm). ORR test was carried out in an O_2 saturated 0.1 M KOH solution. The rotation rate was 1600 rpm, and the I-V curves were recorded by scanning the potential from 0.2 V to 1.05 V (vs RHE).

SEM and XPS characterizations. SEM observations were carried out on a Quanta 200 microscope operating at an accelerating voltage of 30 kV. XPS measurements were conducted on a Kratos XSAM-800 spectrometer with an Mg K_α radiator. The Ag 3d signal was collected and analyzed using the free software XPSPeak.