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Electrooxidation of CO on Ru(0001) and RuO_2(100) Electrode Surfaces

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Abstract: The electrooxidation of CO on Ru (0001) and RuO_2 (100) electrode surfaces were characterized by cyclic voltammetry, AES and RHEED. The CO adlayer was first partially oxidized at 0.8 V, which is controlled by the attack of oxygen species toward the Ru(0001) surface. The remaining CO adlayer oxidation at 0.55 V is related to the combination of CO molecules with oxygen species already located on the surface. In contrast, successive peaks on RuO_2(100) at 0.4 V and 0.72 V are observed, which shows that CO molecules can directly react with two different lattice-oxygen on the surface to carbon dioxide.

Keywords: Ru(0001), RuO_2, CO electrooxidation.

The bond strength and the charge state of oxygen species on the catalyst's surface are considered to govern the activity of an oxidation catalyst. At O/Ru(0001) coverages of 0.25, 0.5, 0.75, and 1 monolayer (2×2)-O, (2×1)-O, (2×2)-3O, and (1×1)-O overlayers are formed, respectively[1]. The O-Ru bond strength decreases by 0.8 eV when the coverage is increased from 0.25 to 1.0 monolayer[2]. Two different oxygen species have been reported for RuO_2: bridge-coordinated O atoms and weakly held O atoms in coordinatively unsaturated Ru atoms (Ru_{cus})[3]. These oxygen species were identified for CO catalytically active sites.

The experiments were performed in a UHV system which consists of a main chamber incorporating LEED, RHEED and AES, and an electrochemical chamber. After the electrochemical measurements, the electrode was characterized in the main UHV chambers, as has been described previously[4].

The oxide layer RuO_2(100) was produced previously by holding the potential at 1.1 V for 2 minutes in 0.1 mol/L $HClO_4$ electrolyte. CO electrosorption was achieved by immersion of Ru(0001) or RuO_2(100) electrodes in a CO-saturated 0.1 mol/L $HClO_4$ solution at potential of -0.1 V for 2 minutes. Standard electrochemical equipment was employed for potential sweeping. All experiments were performed at room temperature and all potentials are given *vs* the Ag/AgCl electrode in saturated KCl solution.

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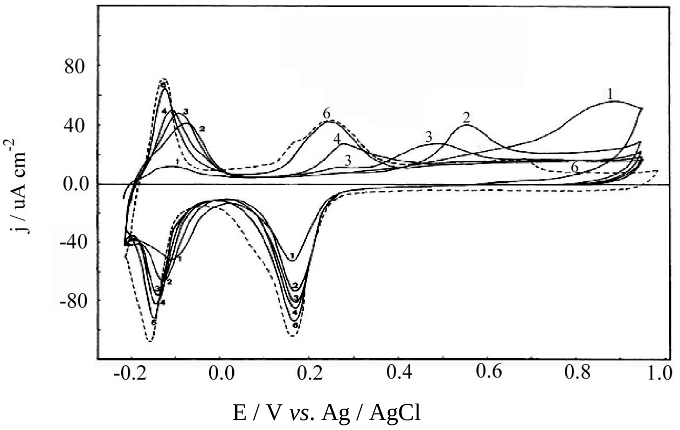
Figure 1 The oxidation of the preadsorbed CO adlayer for Ru(0001) electrode in 0.1 mol/L $HClO_4$ electrolyte

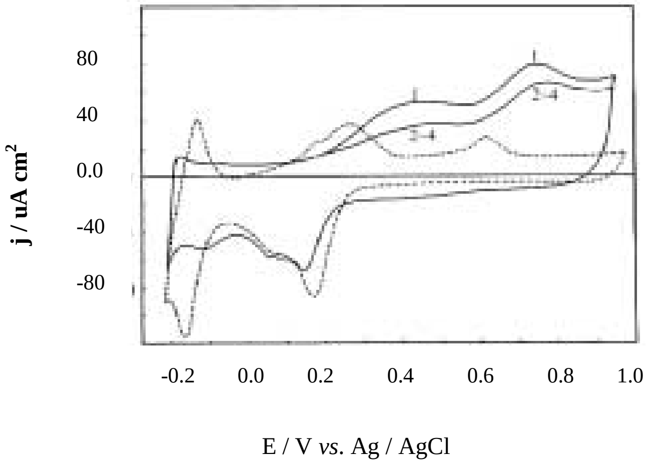


Dashed line shows an UHV-prepared Ru(0001) electrode in pure electrolyte. Sweep rate was 50 mV s^{-1}

Figure 1 shows the cyclic voltammegram for preadsorbed CO electrooxidation on the Ru(0001) electrode in an 0.1 mol/L $HClO_4$ base electrolyte. A pronounced peak appears at 0.8 V on the first anodic scan which is attributed to electrooxidation of CO_{ad} on Ru(0001), since there is no visible anodic peak in the absence of CO on the surfaces (dashed line). On the second cycle, a new anodic peak appeared at a relatively lower potential of 0.55 V where the oxidation of residual CO_{ad} with O_{ad} occurred. These findings indicate that CO oxidation requires coadsorbed oxygen species by the attack of oxygen species toward the Ru(0001) surface. For saturate CO covered Ru(0001) surface, oxygen adsorption can only be enforced at high potential. For lower CO covered Ru(0001) surface, the oxidation sets in much earlier, the shift from 0.8 V to 0.55 V may be due to variations in binding energy for different O_{ad} / CO_{ad} mixtures.

The CO stripping Cyclic voltammegram on RuO_2 surface in CO-saturated 0.1 mol/L $HClO_4$ solution is presented in **Figure 2**. The binding energy of O-Ru_{cus} is only 3.2 eV and therefore significantly lower than that of the bridging O-Ru bonding of 4.6 eV in the RuO_2 surface[3].

Figure 2 The oxidation of the preadsorbed CO adlayer for $RuO_2(100)$ electrode in CO-saturated 0.1 mol/L $HClO_4$ electrolyte.



Dashed line shows RuO_2 electrode in pure electrolyte. Sweep rate was 50 mV s^{-1}

As also corroborated that the bridging O species of RuO_2 is even more weakly bound by 0.5 eV than O in Ru(0001)-(1×1)-O. The low adsorption energy makes O-Ru_{cus} a potentially active species. We may therefore conclude that the present electrochemical data in **Figure 2** is attributed to the interplay between the two different oxygen species on RuO_2 sites. The higher active centers are the coordinatively unsaturated Ru_{cus} atoms. The overpotentials of CO oxidation were obviously lower with the RuO_2 surface than the corresponding Ru(0001) surface. The CO oxidation on RuO_2 can be identified with two reaction channels: (1) the reaction of CO with atomic oxygen, weakly bonded to coordinatively unsaturated Ru_{cus}. And (2) the reaction of CO with the topmost RuO_2 lattice oxygen (O-bridge). Furthermore, the depleted surface oxygen can be restored by continuous scans (as showing **Figure 2**, 2-4 cycles).

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