Reduction of perchlorate on rhodium and its specificity to surface crystallographic orientation

C.K. Rhee, M. Wasberg *, P. Zelenay ** and A. Wieckowski ***

Department of Chemistry, University of Illinois, Urbana, IL 61801, U.S.A.

Received 10 January 1991; accepted 2 July 1991

Catalytic properties of Rh(100), Rh(111) and polycrystalline rhodium electrodes in the process of perchlorate reduction in aqueous media have been studied. The reduction rates obtained under various conditions, as well as results of ultra-high vacuum (LEED, Auger) surface analyses of emersed Rh(100) surfaces, have provided evidence that surface chloride is the main reduction product. A temperature dependent chloride desorption has also been found via measurements of steady-state reduction currents and through chemical analysis of the electrolytic perchlorate solutions. The data demonstrate that under transient conditions, that is, when surface chloride formation determines the reaction rates, the reduction current decreases in the order: Rh(100) > Rh(poly) > Rh(111). Under steady-state conditions the rate order is: Rh(100) ≈ Rh(poly) > Rh(111). The reduction process is pH dependent and, as a prerequisite, requires a contact adsorption of perchlorate on the metal sites. Prospects for using rhodium as a catalyst or catalytic additive in electrocatalysis of inorganic species are discussed.

Keywords: Rhodium; single crystals; electrocatalysis; reduction; perchlorate

1. Introduction

We have recently reported results of electrochemical measurements of an ordered Rh(100) electrode in perchloric acid media which may be of interest to researchers who explore catalytic properties of solid/liquid, electrochemical interfaces [1]. Namely, the observed splitting in the cyclic voltammogram for hydrogen adsorption process on the Rh(100) electrode was interpreted to result from a perchlorate reduction process. The proposed sequence of events based upon the voltammetric behavior involved several steps: (i) a perchlorate reduction to chloride with the rate maximum at the negative end of the double layer

---

* Present address: Abo Academy, Turku-Abo, Finland.

** On leave from the Department of Chemistry, Warsaw University, Warsaw, Poland.

*** To whom the correspondence concerning this manuscript should be addressed.

potential range of rhodium, (ii) the chloride adsorption which prevented an efficient perchlorate reduction under steady-state conditions, and (iii) surface chloride replacement by adsorbed hydrogen in the hydrogen range of the electrode potentials. An additional proviso was made that the chloride released due to the surface hydrogen interference might either diffuse into the bulk of solution or readsorb during the reverse, positive going, voltammetric scan. The data obtained in hydrofluoric acid electrolyte, as well as in sulfuric and hydrochloric acids, were compared with those obtained in perchloric acid, and used as a basis for the proposed interpretation. Prior to our publication [1], the process of perchlorate reduction had been inferred to occur on several high-area metal electrodes based upon chloride determination in perchlorate electrolytes [2–7]. However, the direct effects of the reduction process on short time-scale voltammetric measurements of smooth surfaces had neither been known or anticipated.

In this work, we have studied three rhodium surfaces as catalysts for the perchlorate reduction, and we demonstrate that the Rh(100) face displays the highest catalytic activity. Overall, the reduction rate decreases in the order of Rh(100) > Rh(poly) > Rh(111), or Rh(100) ≈ Rh(poly) > Rh(111), depending on the experimental conditions. Using the Rh(100) electrode and ultra-high vacuum measurements, we provide a direct evidence that chloride resides on the surface after emersion to vacuum. A relatively small dependence of the reduction turnover on temperature shows that the chloride desorption to perchlorate solution most probably determines the overall reaction rate.

2. Experimental

Rh(100) and Rh(111) single crystal surfaces, delivered by the Material Preparation Facility, Cornell University, were oriented, polished and ordered as reported earlier by this laboratory [1,8–12]. A polycrystalline rhodium electrode (Cornell) was cleaned by potential cycling between the hydrogen and oxygen evolution regions after annealing in an H_2 + air flame.

The rate measurements were carried out in a conventional, electrochemical cell using the EG&G PAR 362 voltammetric circuitry. The temperature ranged from 20 to 70 ° C, and was controlled by a water bath with the accuracy of ± 1 ° C. The surface analysis was carried out by the use of an ultra-high vacuum (UHV) instrument combined with electrochemistry in the same apparatus [11,13,14]. The UHV line hosted Auger electron spectroscopy, low energy electron diffraction, LEED, and an ion gun for argon ion-bombardment cleaning procedure. A cylindrical mirror analyzer was used for the Auger measurements. The base pressure of the UHV instrument was 10^{-11} Torr. The manipulator which transferred the electrode between the vacuum and solution phase, to which the electrode was attached via resistively heated wires, was controlled by an electric step motor. The manipulator was equipped with a stainless steel bellow which secured the vacuum environment in the two basic parts of the instrument: the electrochemistry chamber and the vacuum chamber. The electrochemical cell design was reported in ref. [13].

Wherever indicated below, the solutions were analyzed for the presence of chloride by the use of mercuric complexometric titration. The detection limit for chloride determination by this method was 2×10^{-5} M. The potentials in this work are reported against the Ag/AgCl electrode in 1 M NaCl solution. All solutions were made of Millipore water and ACS reagent grade and Ultrex ultrapure chemicals (VWR), and were purged with oxygenfree nitrogen (Linde).

3. Results and discussion

STEADY-STATE VOLTAMMETRY

Cyclic voltammograms of Rh(100), Rh(111) and polycrystalline rhodium electrodes taken in 0.1 M perchloric acid, 0.1 M hydrofluoric acid, and in 0.1 M perchloric acid containing 0.1 mM of sulfuric acid solutions are shown in figs. 1, 2 and 3, respectively. As expected from the data of ref. [1], all voltammograms obtained in perchloric acid, figs. 1-a, 2-a and 3-a, are different from those obtained in hydrofluoric acid, figs. 1-b, 2-b and 3-b. This shows that heterogeneous reduction of perchlorate is not only characteristic of Rh(100) [1], but for all surfaces studied in this work.

In order to develop a quantitative grasp of the perchlorate reduction rates, clean, Cl-free rhodium surfaces were exposed to perchloric acid electrolytes and the reduction current was measured under voltammetric (transient) conditions.

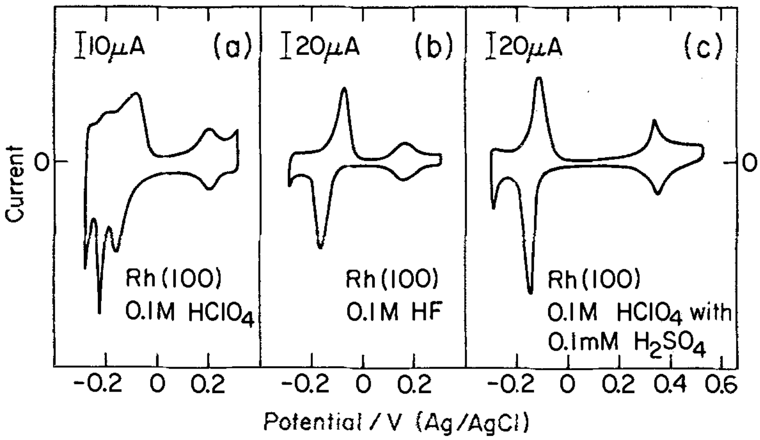


Fig. 1. Cyclic voltammograms of the Rh(100) electrode in various supporting electrolytes. Scan rate 50 $mV \cdot s^{-1}$.

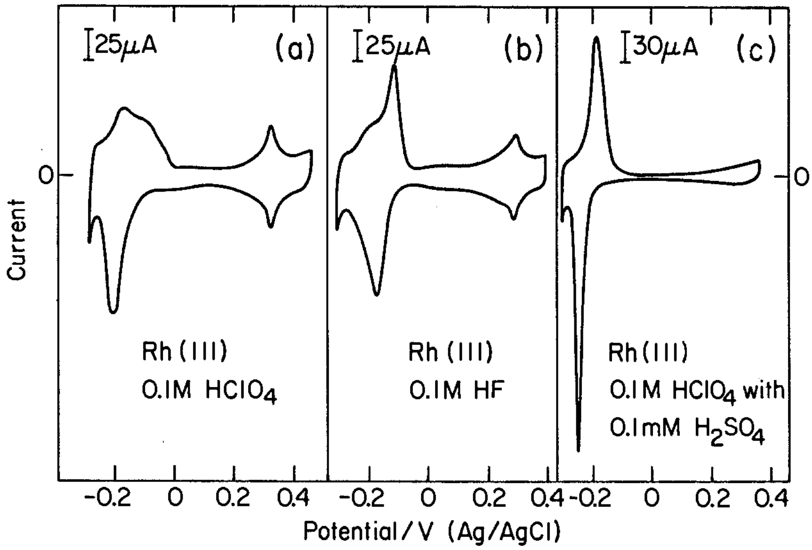


Fig. 2. Cyclic voltammograms of the Rh(111) electrode in various supporting electrolytes. Scan rate 50 $mV \cdot s^{-1}$.

The experiments begun with rhodium surfaces covered by chemisorbed carbon monoxide [1]. Before measurements of the reduction current a protective layer of the surface CO was voltammetrically stripped off the surface and chloride-free rhodium sites were exposed to the solution, fig. 4. The peak observed on the positive-going scan at about 0.4 V for the three surfaces is due to the surface CO stripping. On the reverse run, the observed increase in the negative current that begins at 0.05 V is due to perchlorate reduction and the current decline below −0.05 V, due to chloride adsorption, as discussed before [1]. That is, the current-potential peak in the potential range of 0.05 V to −0.15 V is assigned to the perchlorate reduction process. The comparison of the data of fig. 4 indicates that the reduction current-potential peak at −0.05 V is well-developed only

Table 1
Maximum currents, reaction turnovers and apparent activation energies for perchlorate reduction at rhodium electrodes.

	Rh(100)	Rh(poly)	Rh(111)
	Transient conditions		
Current density at −0.05 V ($\mu A \cdot cm^2$) [a]	81	63	30
	Steady-state conditions		
Reaction turnover at −0.05 V ($\times 10^3$) [b]	13	13	1.6
Apparent activation energy ($kJ \cdot mole^{-1}$) [c]	41	41	18

[a] See fig. 4.
[b] At 70 °C, see fig. 8.
[c] See fig. 8.

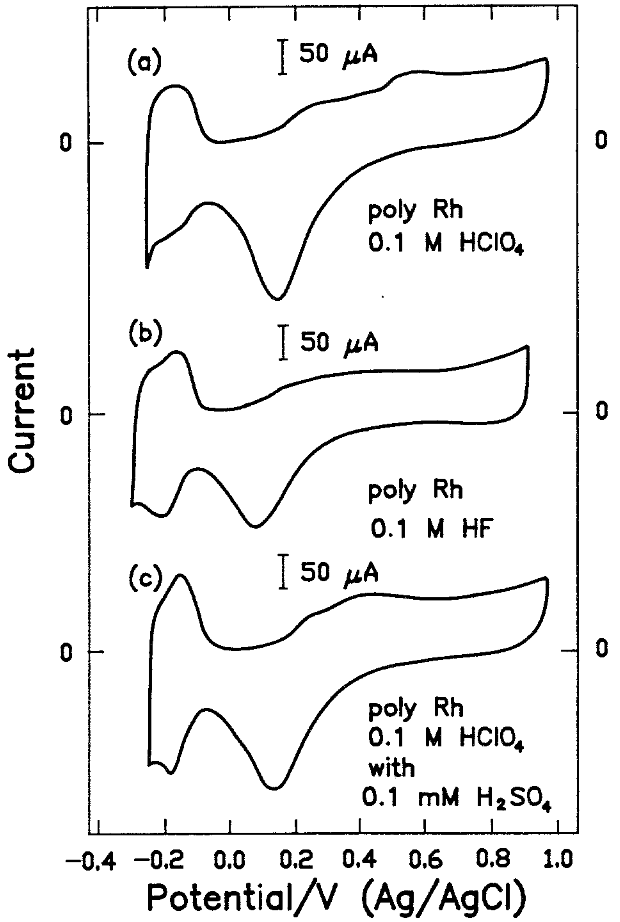


Fig. 3. Cyclic voltammograms of the Rh(poly) electrode in various supporting electrolytes. Scan rate 50 $mV \cdot s^{-1}$.

with the Rh(100) electrode, and that its amplitude decreases in the order: (100), (poly), (111). We therefore conclude that the reduction rate measured under the voltammetric transient conditions falls into the same order. The maximum current densities for perchlorate reduction, measured after CO stripping and the scan reversal, are summarized in table 1.

VACUUM CHARACTERIZATION OF Rh(100) ELECTRODE

Several Auger spectra and LEED patterns will be presented below to provide evidence for chloride formation on rhodium surfaces in perchlorate media. The Rh(100) surface, which is the most active, was chosen for the measurements.

Fig. 5-a shows the Auger spectrum of the clean surface following a standard ion bombardment/annealing procedure [10]. All Auger transitions seen in this

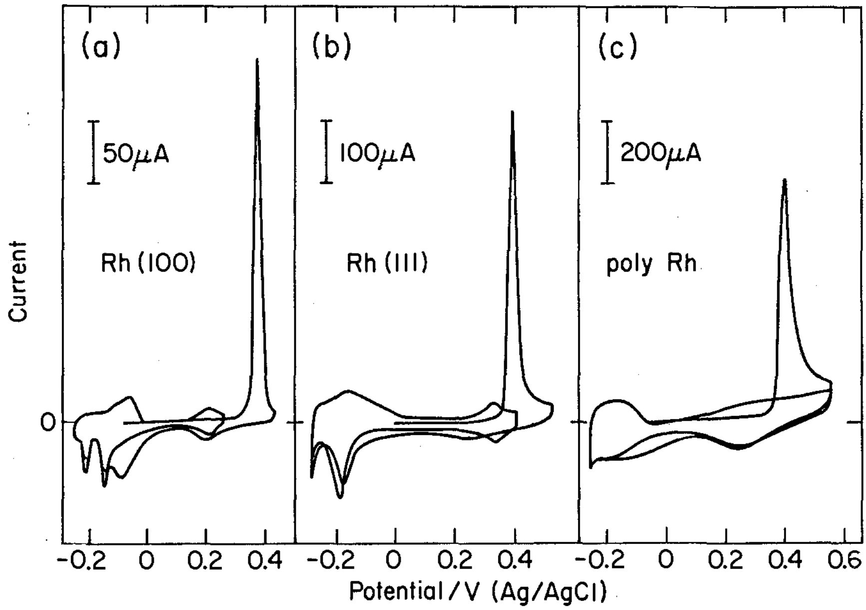


Fig. 4. Electrooxidation of a saturation coverage of carbon monoxide adsorbed on rhodium electrodes. Carbon monoxide was adsorbed from CO-saturated 0.1 M $HClO_4$. Scan rate 50 $mV \cdot s^{-1}$.

figure can be assigned to the element rhodium, thereby indicating that carbon and boron, rhodium main contaminants, were removed from the surface [15]. The vacuum prepared Rh(100) surface displays a regular (1 × 1) LEED pattern, fig. 6-a. The Auger spectrum shown in fig. 5-b was measured after: (i) a steady-state voltammogram was obtained after multiple cycling in 0.1 M $HClO_4$ (which provides a stabilized surface, fig. 1-a), (ii) the cyclization was interrupted at the hydrogen evolution edge of −0.23 V, (iii) the electrode was rinsed 3 times with water, and (iv) the electrode was emersed to vacuum. In this spectrum, as in all other spectra shown in fig. 5, the Auger transitions are seen that can be ascribed to surface chloride and surface oxygen of varied proportions. (All the data were obtained after extrapolation of the Auger peak-to-peak heights to zero time.) The spectrum shown in fig. 5-c was obtained after electrode emersion at −0.05 V, that is, where the rate of perchlorate reduction reaches its maximum (ref. [1] and fig. 4-a). In figs. 5-d and 5-e, the emersion potentials were 0.30 and 1.30 V, which correspond to the end of the rhodium "butterfly" (assignable to the first oxidation stage of this metal [11]) and to the oxygen evolution edge, respectively. In the latter case, the surface was covered by approximately 2.5 monolayers of rhodium oxide, assuming that Rh_2O_3 represents the stable rhodium oxide stoichiometry [16].

Finally, fig. 5-F contains the Auger data obtained after (i) electrode "immersion" from vacuum to the electrolyte (the rest potential was 0.48 V), (ii) a single

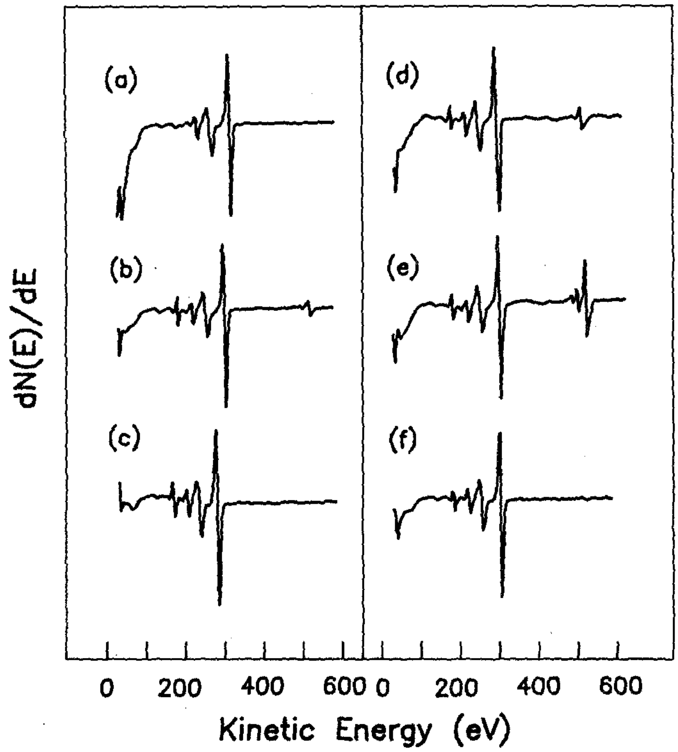


Fig. 5. Auger spectra of Rh(100) surfaces: (a) before transfer to electrolytic solution; (b) after emersion from 0.1 M $HClO_4$ at −0.23 V; (c) after emersion at −0.05 V; (d) after emersion at 0.30 V, (e) after emersion at 1.3 V and (f) after emersion at −0.05 V. Spectra a–e were obtained with stabilized Rh(100) surfaces and spectrum f with a single-scan treated surface (see text). Beam energy 3 keV.

potential scan from the rest potential to the perchlorate reduction maximum (−0.05 V), and (iii) the electrode emersion to vacuum. Such a linear scan voltammogram and subsequent cyclic, current-potential profiles are demonstrated in fig. 7. The voltammetric behavior shown in fig. 7 is again consistent with our interpretation of the perchlorate reduction process on Rh(100). In particular, the first negative-going scan shows a distinctive −0.05 V feature assignable to perchlorate reduction on the Cl-free Rh(100) surface (vide supra). The remaining scans, as affected by chloride adsorption, show the development of Rh-Cl sites which are being gradually occupied by hydrogen through a Cl-displacement process, fig. 7-a, a decrease in hydrogen adsorption on the Cl-free sites, fig. 7-b, and a characteristic decrease in perchlorate reduction maximum, fig. 7-c [1].

The Auger peak-to-peak heights (H) at 180 eV and 511 eV for surface Cl- and O-species, respectively, were normalized to the rhodium peak-to-peak height at 303 eV [17], to produce the peak-to-peak ratios (H/H) for several emersion potentials, table 2. How much chloride and oxygen is held by the surface can be estimated by knowing that 56.6 $\mu C \cdot cm^{-2}$ of electric charge is transferred between 0.00 and 0.30 V during the surface oxidation of the Rh(100) electrode, fig. 1-c. This charge gives 0.32 coverage by surface OH at $E = 0.30$ V,

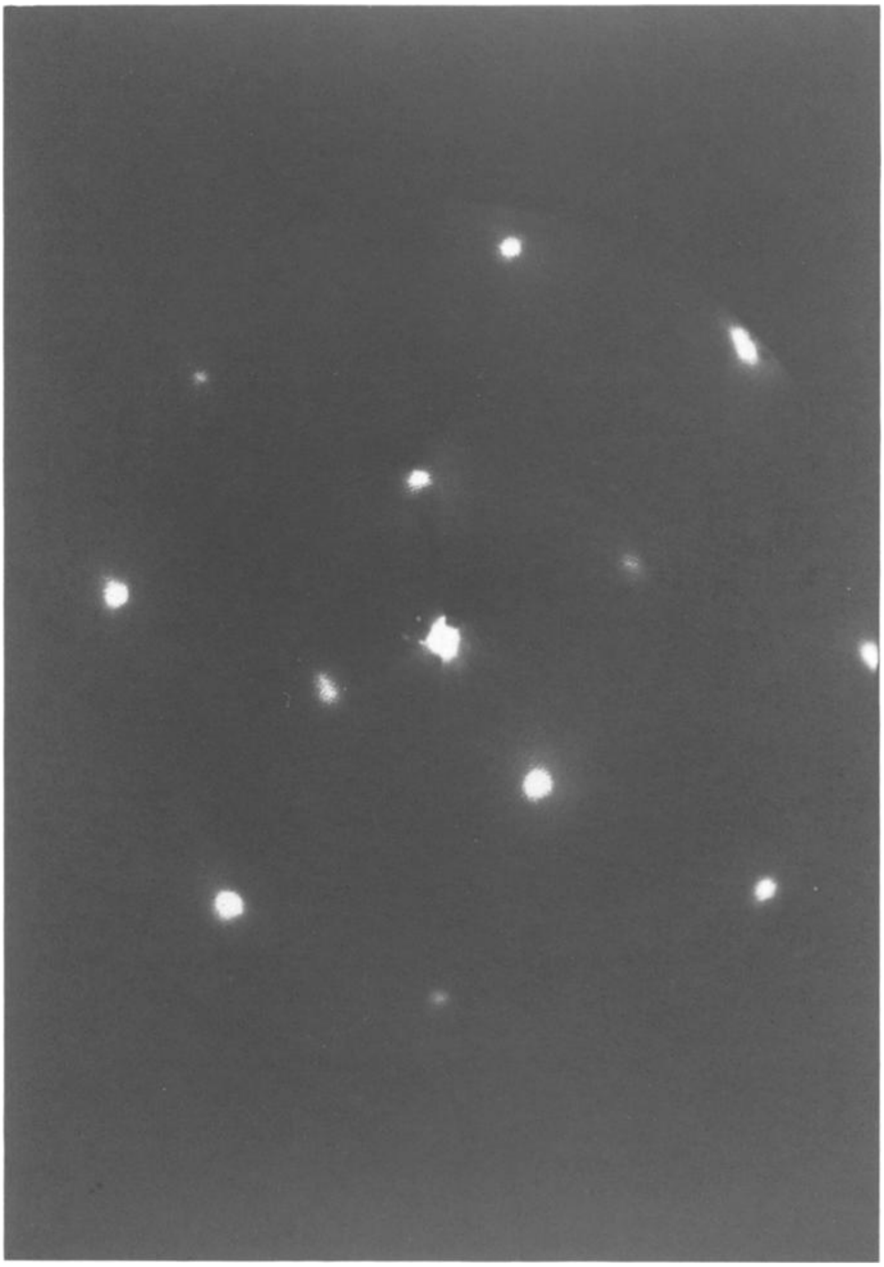
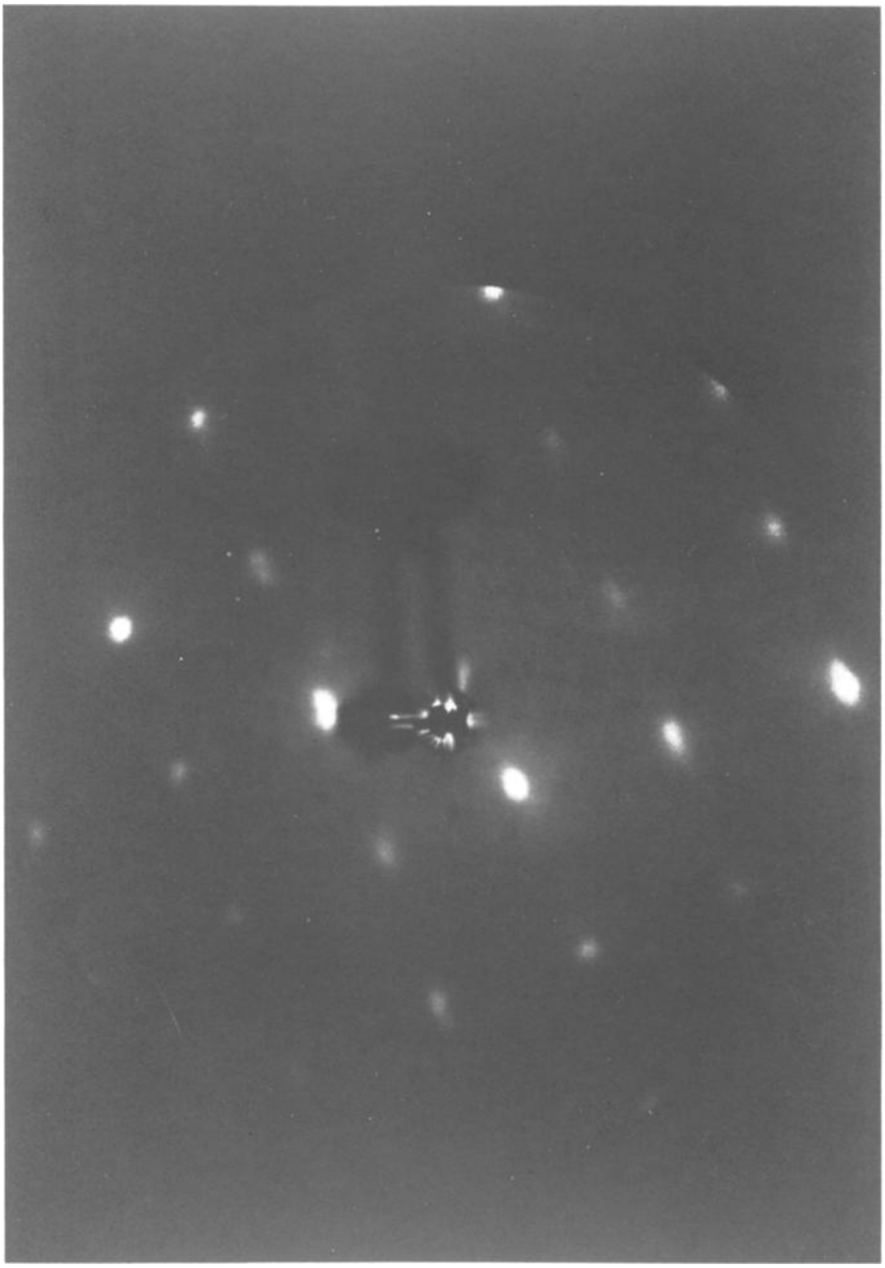

(a)

Fig. 6. LEED patterns of the following surface structures: (a) Rh(100)(1 × 1), before transfer to solution, and (b) Rh(100)*c*(2x2)-Cl after emersion from 0.1 M $HClO_4$ at −0.05 V (see text). Beam energy 141.8 eV.



(b)

Fig. 6. (continued)

and corresponds to the ratio of the Auger signals of O to Rh, (H_O/H_{Rh}, table 2) of 0.28. Using the sensitivity factors for chloride and oxygen as 1.1 and 0.5, respectively [17], the coverages of surface oxygen and chloride were calculated and added to table 2. (The coverages here are tantamount to packing densities,

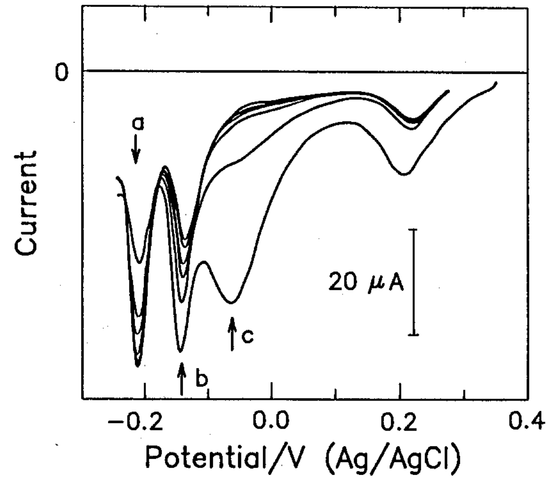


Fig. 7. The evolution of a voltammetric profile of clean, UHV-prepared Rh(100) surfaces after immersion in 0.1 M $HClO_4$. Shown is the negative half of the voltammetric record. The evolution direction is indicated by arrows. Scan rate 50 $mV \cdot s^{-1}$.

the number of oxygen or chloride species per the number of platinum surface atoms.) The atomic ratios of the surface oxygen to chloride are also included in this table. While the amount of the Cl-species held by the surface after a single scan, fig. 7, is similar to that found on the stabilized (multiple cycled) surface, fig. 1-A, the coverage by the surface oxygen is four times higher. This shows that the immersed Rh(100) surface is not fully reduced upon the first negative-going

Table 2
Auger spectroscopic data of the Rh(100) electrode emerged from 0.1 M $HClO_4$ solution at various potentials [a]

Voltammetric pretreatment [b]	Emersion potential (V)	H_O/H_{Rh} [c]	H_{Cl}/H_{Rh}	Θ_O	Θ_{Cl}	Θ_O/Θ_{Cl}
multiple scans [d]	−0.23	0.09	0.17	0.20	0.17	1.2
	−0.05 [e]	0.011	0.19	0.02	0.19	0.1
	0.30	0.13	0.14	0.28	0.14	2.0
	1.30	0.46	0.15	1.01	0.15	6.7
single scan [d,f]	−0.05	0.04	0.20	0.09	0.20	0.5

[a] See fig. 5 and 7.
[b] Before emersion.
[c] *H* stands for peak-to-peak heights of the corresponding Auger transitions.
[d] See text.
[e] Potential of reduction maximum.
[f] See fig. 7.

scan down to −0.05 V, as expected from the corresponding vacuum data for the Rh(111) electrode [11].

At −0.05 V, that is, at the perchlorate reduction maximum, the Θ_O/Θ_{Cl} ratio is equal to 0.1, table 2. The Θ_O/Θ_{Cl} ratio for adsorbed perchlorate, obtained using the same Auger sensitivity factors for oxygen and chloride as above, and disregarding the attenuation of Auger electrons in the surface zone, is equal to 1.82. The 0.1 ratio shows that at −0.05 V the surface is practically free of oxygen. At the same time, the coverage by Cl-species is 0.19, table 2. These data provide a complete *ex situ* evidence for perchlorate reduction to surface chloride on the Rh(100) electrode at the electrode potential of the reduction maximum. The chloride coverage due to perchlorate reduction can also be evaluated using *in situ* voltammetric data shown in fig. 1-a. Using this method, and assuming that the charge measured in the potential range of 0.05 to −0.15 V is due to a complete reduction of perchlorate to surface chloride, the coverage by Cl-species is 0.14. It appears that both the *in situ* and *ex situ* results are quite consistent if such a complete reduction is concluded.

As postulated before [1] adsorbed chloride is removed from the electrode at the onset of hydrogen evolution, that is at −0.23 V. At the same time the Auger analysis shows that Cl and O species are still present at the surface, table 2. However, the Θ_O/Θ_{Cl} ratio obtained at −0.23 V is much higher than that at −0.05 V, and is equal to 1.2, table 2. Most probably, at such a negative electrode potential, a submonolayer of perchlorate is sufficiently strongly held by the substrate to withstand evacuation and be detected by the Auger spectroscopy. The fact that the Θ_O/Θ_{Cl} ratio is still lower than 1.82, may indicate that an attenuation of the Auger signals for some of the perchlorate oxygens is quite efficient. Since adsorption of some chloride on the top of adsorbed hydrogen layer cannot be excluded, the interpretation of the data obtained at this extreme potential cannot, at present, be conclusive.

Emersion of stabilized Rh(100) the electrode to vacuum at any potential between −0.23 to 0.30 V produced a diffuse (1 × 1) LEED pattern. However, if the single-scan pretreated surface, figs. 5-f and 7, was emersed at −0.05 V, a $c(2\times2)$ LEED pattern appeared on a considerable background. After Auger electron exposure or after a gentle heating, the background intensity was reduced to yield a sharp $c(2\times2)$ pattern shown in fig. 6-b. The Auger analysis indicated that the coverages by chloride and oxygen were: 0.09 and 0.20, respectively. Since this is considerably less than expected for the close-packed $c(2\times2)$ surface structure, we may conclude that only islands of the Cl and O species gave rise to the LEED pattern shown in fig. 6-b.

REACTION TURNOVERS AND TEMPERATURE MEASUREMENTS

A negative current was measured at room temperature when rhodium electrodes were polarized in 0.1 M $HClO_4$ at −0.05 V, that is, at the potential of

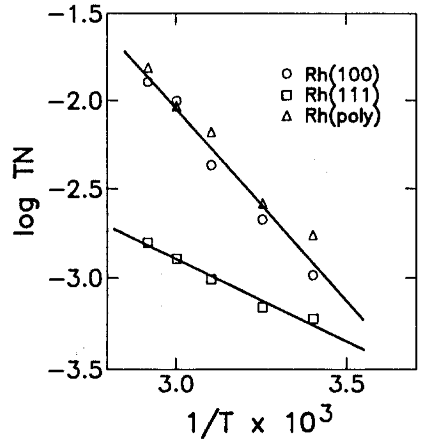


Fig. 8. Arrhenius plots for reduction of perchlorate at rhodium electrodes in 0.1 M $HClO_4$ at −0.05 V (TN stands for turnover number).

the reduction rate maximum, fig. 4. The following observations demonstrate that this current, which increased with the increase in solution temperature, can easily be assigned to a steady-state perchlorate reduction to solution chloride. First, no negative currents at −0.05 V were observed with 0.1 M hydrofluoric acid electrolyte either at room temperature, or at 50 °C. Second, 2×10^{-4} M solution chloride was detected after 10 hours of electrolysis at a high area polycrystalline rhodium electrode (400 cm^2), which was obtained by electrodeposition of rhodium on gold. At the same time, no chloride was found in the starting 0.1 M $HClO_4$ solution. The steady-state reduction current roughly accounts for the amount of chloride produced if one assumes that a total reduction of perchlorate to chloride takes place. If so, the reaction turnovers and their temperature dependencies may be determined from the reduction currents assuming an eight electron reaction stoichiometry. The corresponding data for the three Rh surfaces plotted in Arrhenius coordinates in the temperature range of 22–70 °C are shown in fig. 8. The turnover numbers obtained at 70 °C, and the apparent activation energies, are added to the data in table 1.

The inspection of the steady-state reduction data, fig. 8 and table 1, shows that while the reaction turnovers for Rh(100) and Rh(poly) taken at several temperatures are similar, that for Rh(111) is much lower. Therefore, the perchlorate reduction rate changes in the order of Rh(100) ≈ Rh(poly) > Rh(111). The apparent activation energies, table 1, are 41 $kJ \cdot mole^{-1}$ for Rh(100) and Rh(poly), and ca. 18 $kJ \cdot mole^{-1}$ for Rh(111). Both values are low, especially that for the Rh(111), and are below the typical values for a heterogeneous, catalytic bond splitting of inorganic anions or molecules reacting at solid/liquid, catalytic interfaces (ref. [18], and references therein). We may tentatively account for our observation by assuming that the reduction current is controlled by the availability of catalytic sites, which are determined by the coverage of chloride. Since adsorption of chloride on metal surfaces is reversible [7], the steady-state chloride coverage under our experimental conditions will tend to be lower at higher temperature. This, in turn, will supply more surface sites for perchlorate reduction and provide more catalytic current. If, indeed, this interpretation properly accounts for the surface phenomena studied in this work, the meaning of the activation energies given in table 1 is purely formal. That is, the temperature dependency of the reaction rates do not represent activation processes but reflect the indicated catalytic site release mechanism. To be consistent with this latter mechanism, we must postulate that chloride is adsorbed more strongly on Rh(111) than on the other surfaces, and its coverage is affected less by the increase in temperature. This conclusion will have to be confirmed by independent measurements. At this stage, we may also expect that void of the chloride adsorption, the yield of the perchlorate reduction process to solution chloride would be higher than observed in this work.

THE OVERALL REDUCTION MECHANISM

Since adsorption of chloride and hydrogen, figs. 4 and 7, and bisulfate, fig. 1-c, slows and eventually stops the reduction, we conclude that a contact adsorption of perchlorate on free rhodium sites is required to initiate the reduction. Since the reduction process begins well before adsorbed hydrogen is formed, fig. 2, the overall reduction scheme is:

$$(ClO_4^-)_{aq} = (ClO_4^-)_{ad} \tag{1a}$$

$$(ClO_4^-)_{ad} + 8H_3O^+ + 8\,e^- = (Cl^-)_{(ad\ or\ aq)} + 12H_2O \tag{1b}$$

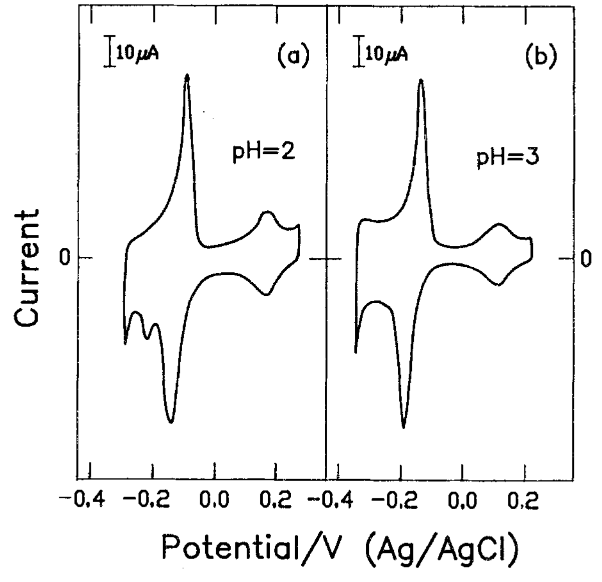


Fig. 9. Cyclic voltammograms for the Rh(100) electrode at two solution pHs. The concentration of ClO_4^- ions was 0.1 M. Scan rate 50 mV·s^{-1}.

where chloride may either be adsorbed (ad) or diffuse to the bulk of solution (aq). Scheme 1 also shows that the chloride production, and its interference with rhodium voltammetry, should be dependent on solution pH. The voltammetric data shown for Rh(100) in fig. 9 indicate that this is indeed the case. The current-potential peak at -0.2 V, which appears on the voltammogram as a result of the replacement of adsorbed chloride by adsorbed hydrogen [1], is substantially reduced at $\mathrm{pH} = 2$ and disappears at $\mathrm{pH} = 3$. Actually, at $\mathrm{pH} = 3$, a replica of the cyclic voltammogram obtained in clean HF is observed, cf. the data in fig. 1-b. In summary, whereas we did not attempt to delineate the sequence of the consecutive steps for the reduction reaction, we may conclude that the reactions represented by scheme 1 are consistent with all the experimental details collected in this work.

ELECTROCATALYSIS WITH RHODIUM ELECTRODES

The search for some unique catalytic behavior of rhodium electrodes with respect to solution species (ref. [12] and references therein) parallels a corresponding activity in the gas phase surface science research [19–24]. The electrochemical work, that begun with some now well recognized investigations [2–6], has only partially been successful. For instance, while Koch et al. provided evidence that an enhancement in methanol electrooxidation was observed with respect to platinum electrode when 20% at. per cent of rhodium was added to platinum [25], Weaver et al., demonstrated that rates of electro-oxidation processes of CO and some other organic molecules on rhodium are lower than on platinum [26].

At the same time, it is well known that rhodium exhibits a pronounced surface activity toward anion adsorption [1,3,9,12]. Recently, using single the crystal Rh(111) electrode, ordered and disordered, as well as polycrystalline rhodium, Zelenay et al. have observed a distinctive crystallographic specificity in bisulfate adsorption [12]. We believe that the observation concerning perchlorate reduction on rhodium is a consequence of the general activity which rhodium exerts towards inorganic anions. Consequently, the crystallographic specificity observed in perchlorate reduction is most probably related to the one observed in the anion adsorption processes. Therefore, based upon the present results, as well as upon the earlier work [1,12], we conclude that considering rhodium electrodes as a catalyst, or element rhodium as a catalytic additive, in heterogeneous inorganic electrocatalysis is well in place.

4. Conclusions

Unlike most noble metals, such as gold and platinum, which are barely active in the perchlorate reduction, rhodium appears to have electronic configuration that facilitates an efficient surface reduction of perchlorate to chloride. As shown in this paper, the Rh(100) orientation has the most appropriate surface geometry in the transformation of perchlorate to the reduction product. The catalytic specificity observed in this work may reflect differences in the heats and entropies of adsorption of perchlorate and/or chloride at various crystallographic planes of this metal. Whereas the tendency of chloride to become adsorbed on metal electrodes is well-established, the same tendency for perchlorate adsorption has not yet been confirmed. However, a logical consistency of our considerations calls for an assumption that perchlorate is involved in a contact adsorption on rhodium. This inference must be checked by conducting quantitative *in situ* surface measurements, which are planned in our laboratory. Since perchlorate is a very popular electrolyte in investigations of solid/liquid interfaces, we believe that the results of our work are of interest to many electrochemists and surface scientists who operate in aqueous media. Likewise, we postulate that the process of perchlorate reduction discloses some unique catalytic possibilities of rhodium in heterogeneous electrocatalysis with participation of inorganic compounds. This warrants further electrochemical investigations of rhodium, including studies of rhodium single crystal electrodes.

Acknowledgement

Numerous discussions concerning this project with Professor G. Horányi of the Hungarian Academy of Sciences, Budapest, is highly appreciated. This work was supported by the National Science Foundation, the Grant No. NSF-DMR-89-20538, administered by the Materials Research Laboratory, Urbana, Illinois. One of us (C.K.R.) acknowledges support by the Air Force Office of Scientific Research (AFOSR-89-0368) to his research at Urbana.

References

[1] C.K. Rhee, M. Wasberg, G. Horányi and A. Wieckowski, J. Electroanal. Chem. 291 (1990) 281.
[2] S. Yu. Vasina and O.A. Petrii, Electokhimiya 6 (1970) 242.
[3] M.S. Chemeris, A.G. Stromberg and Yu. B. Vasil'ev, Electrokhimiya 11 (1973) 560.
[4] C. Pallotta, N.R. De Tacconi and A.J. Arvia, J. Electroanal. Chem. 159 (1983) 201.
[5] M. Sánchez-Cruz, Ma. J. Gonzalez-Tejera and Ma. C. Villamañan, Electrochim. Acta 30 (1985) 1563.
[6] F. Colom and M.J. Gonzalez-Tejera, J. Electroanal. Chem. 190 (1985) 243.
[7] G. Horányi and E.M. Rizmayer, J. Electroanal. Chem. 198 (1986) 379.
[8] M. Hourani and A. Wieckowski, J. Electroanal. Chem. 227 (1987) 259.
[9] M. Hourani and A. Wieckowski, J. Electroanal. Chem. 244 (1988) 147.
[10] M. Wasberg, M. Hourani and A. Wieckowski, J. Electroanal. Chem. 278 (1990) 425.
[11] M. Hourani, M. Wasberg, C.K. Rhee and A. Wieckowski, Croat. Chem. Acta. 63 (1990) 373.

[12] P. Zelenay, G. Horányi, C.K. Rhee and A. Wieckowski., J. Electroanal. Chem. 300 (1991) 499.

[13] M. Wasberg, L. Palaikis, S. Wallen, M. Kamrath and A. Wieckowski, J. Electroanal. Chem. 256 (1988) 51.

[14] D. Zurawski, M. Wasberg and A. Wieckowski, J. Phys. Chem. 94 (1990) 2076.

[15] L.H. Dubois, J. Chem. Phys. 77 (1982) 5228.

[16] J.F. Llopis, I.H. Tordesillas and E.J. Bard, eds., *Encyclopedia of Electrochemistry of the Elements*, Vol. VI, (Dekker, New York, 1976) Ch. VI-9.

[17] G. Ertl and M. Küppers, in: *Low Energy Electrons and Surface Chemistry* (Verlag Chemie, Weinheim, 1974) Ch. 2 and 3.

[18] P. Zelenay, B.R. Scharifker and J.O'M. Bockris, J. Electrochem. Soc. 133 (1986) 2262.

[19] B.A. Sexton and G.A. Somorjai, Surf. Sci. 71 (1978) 519.

[20] C. Lee and L.D. Schmidt, J. Catal. 101 (1986) 123.

[21] J.T. Kummer, J. Phys. Chem. 90 (1986) 4747.

[22] R.W. McCabe and Chor Wong, J. Catal. 121 (1990) 422.

[23] R.F. Van Slooten and B.E. Nieuwenhuys, J. Catal. 122 (1990) 429.

[24] A. Benedetti, A. Carimati, S. Marengo, S. Martinengo, F. Pinna, R. Tessari, G. Strikul, T. Zerlia and L. Zanderrighi, J. Catal. 122 (1990) 330.

[25] D.F.A. Koch, D.A.J. Rand and R. Woods, J. Electroanal. Chem. 70 (1976) 73.

[26] L.-W.H. Leung and M.J. Weaver, J. Phys. Chem. 93 (1989) 7218.