# MODERN ASPECTS OF ELECTROCHEMISTRY

### No. 42

### Modern Aspects of Electrochemistry

#### Topics in Number 41 include:

- Solid State Electrochemistry, including the major electrochemical parameters needed for the treatment of electrochemical cells as well as the discussion of electrochemical energy storage and conversion devices such as fuel cells
- Nanoporous carbon and its electrochemical application to electrode materials for super capacitors in relationship to the key role nanoporous carbons have played in the purification of liquids and the storage of energy
- The analysis of variance and covariance in electrochemical science and engineering
- The use of graphs in electrochemical reaction networks, specifically: (1) reaction species graphs, (2) reaction mechanism graphs, and (3) reaction route graphs

#### Topics in Number 40 include:

- Polymer Electrolyte Membrane (PEM) fuel cell bipolar plates, discussion of the difficulties associated with confronting bipolar plate development
- The use of graphs in electrochemical reaction networks with focus on analysis of variance (ANOVA) observation methods
- Nano-materials in lithium ion battery electrode design, presentation of a plasma-assisted method to create a carbon replica of an alumina template membrane
- Direct methanol fuel cells, extensive discussion and review of various types of fuel cells and advances made in the performance of DMFC's since their inception
- Direct simulation of polymer electrolyte fuel cell catalyst layers, presentation of a systematic development of the direct numerical simulation

# MODERN ASPECTS OF ELECTROCHEMISTRY

# No. 42

Edited by

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#### Preface

This volume analyzes and summarizes recent developments in several key interfacial electrochemical systems in the areas of fuel cell electrocatatalysis, electrosynthesis and electrodeposition. The six Chapters are written by internationally recognized experts in these areas and address both fundamental and practical aspects of several existing or emerging key electrochemical technologies.

The Chapter by R. Adzic, N. Marinkovic and M. Vukmirovic provides a lucid and authoritative treatment of the electrochemistry and electrocatalysis of Ruthenium, a key element for the development of efficient electrodes for polymer electrolyte (PEM) fuel cells. Starting from fundamental surface science studies and interfacial considerations, this up-to-date review by some of the pioneers in this field, provides a deep insight in the complex catalytic-electrocatalytic phenomena occurring at the interfaces of PEM fuel cell electrodes and a comprehensive treatment of recent developments in this extremely important field.

Several recent breakthroughs in the design of solid oxide fuel cell (SOFC) anodes and cathodes are described in the Chapter of H. Uchida and M. Watanabe. The authors, who have pioneered several of these developments, provide a lucid presentation describing how careful fundamental investigations of interfacial electrocatalytic anode and cathode phenomena lead to novel electrode compositions and microstructures and to significant practical advances of SOFC anode and cathode stability and enhanced electrocatalysis.

The electrocatalysis of the electrochemical reduction of  $CO_2$ , a reaction of great potential importance for the future, is treated in an authoritative chapter by Y. Hori, who for many years has been a leading expert in this area. The Chapter reviews critically the plethora of experimental investigations of  $CO_2$  reduction on different metals and provides deep and useful insight about the fundamental mechanisms leading to dramatically different product selectivity on different metals.

The Chapter by E. Gileadi and N. Eliaz provides a lucid and thorough treatment of the interfacial phenomena of electrodeposition and codeposition. The authors, who are internationally renowned experts in this important field, provide a deep and concise survey of experimental and theoretical findings and point out several important codeposition phenomena which defy existing theoretical treatments and show the necessity for novel theoretical analyses of the electrode-electrolyte interface, accounting for ion rather than electron transfer at the electrochemical interface.

The great usefulness of scanning tunneling microscopy (STM) for a better understanding of catalysis, electrocatalysis and electrodeposition at the fundamental level is presented by M. Szklarczyk, M. Strawski and K. Bieńkowski in a concise historical review which summarizes key landmarks in this important area and presents some of the almost limitless opportunities for the future.

The key role of electrochemistry in several important emerging technologies, such as electrodeposition and electroforming at the micro and nano level, semiconductor and information storage, including magnetic storage devices, and modern medicine, is described lucidly by M. Schlesinger in an authoritative Chapter. These new "high tech" electrochemical applications, presented by an author with great relevant experience open numerous challenges and opportunities for the electrochemist of the 21st century.

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#### Some Recent Studies in Ruthenium Electrochemistry and Electrocatalysis

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#### I. INTRODUCTION

Ruthenium is a metal of a considerable importance in electrochemical science and technology. It is a catalyst or co-catalyst material in Pt-Ru alloys for methanol- and reformate hydrogenoxidation in fuel cells, while ruthenium oxide, a component in chlorine-evolution catalysts, represents an attractive material for electrochemical supercapacitors. Its facile surface oxidation generates an oxygen-containing species that provides active oxygen in some reactions. Ru sites in Pt-Ru catalysts increase the "CO tolerance" of Pt in the catalytic oxidation-reaction in direct methanol fuel cells (DMFC) and in reformate hydrogen-oxidation in proton exchange membrane fuel cells (PEMFC). The mechanism of Ru action is not completely understood, although the current consensus revolves around the so-called "bifunctional mechanism" wherein Ru provides oxygenated species to oxidize CO that blocks Pt sites, and has an electronic effect on Pt-CO interaction.

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#### a) Ru(0001)

b) Ru(1010)



Figure 1. Structural model of (a) Ru(0001); (b) two terminations of the Ru( $10\overline{1}0$ ) surface.

While various studies of polycrystalline Ru go back several decades,<sup>1,2,3</sup> those involving single crystal surfaces and the structural sensitivity of reactions on Ru surfaces emerged only recently. Using well-ordered single crystalline surfaces brings useful information as the processes on realistic catalysts are far too complex to allow identification of the microscopic reaction steps. In this article, we focus on progress in model systems and conditions, such as electrochemistry and electrocatalysis on bare and Pt-modified well-ordered Ru(0001) and Ru( $10\overline{1}0$ ) single-crystal surfaces. We also review the current understanding of the mechanistic principles of Pt-Ru systems and a new development of a Pt submonolayer on Ru support electrocatalyst.

Ruthenium crystallizes in a hexagonal close-packed structure, (hcp). Figure 1 shows the two single crystal surfaces of Ru. The Ru(0001) surface possesses the densest, i.e., hexagonal arrangement of atoms, Fig. 1a. The other plane, Ru(1010), can have one of the two terminations of the surface atoms, Fig. 1b. One termination can be described as a stepped surface with a trigonal arrangement of atoms in two-atom-long terraces with a step of the same orientation; the other termination is a square-symmetrical arrangement of atoms in steps. In the faced-centered cubic (*fcc*) system, these three structures are uniquely defined and labeled as (111), (110), and (210), respectively.

#### II. PREPARATION OF WELL-ORDERED Ru SINGLE-CRYSTAL SURFACES

For over three decades, a procedure has been known for preparing well-ordered Ru single-crystal surfaces in ultra-high vacuum (UHV).<sup>4</sup> It involves Ar<sup>+</sup> sputtering at room temperature, followed by several cycles of oxygen adsorption (at 800 K) and desorption (at 1700 K), both in an oxygen atmosphere of 10<sup>-7</sup> Torr; finally, the crystal is flash heated to 1700 K at UHV to remove traces of oxygen from the Ru surface.<sup>4</sup> One of the first reports on voltammetry and in situ infrared (IR) spectroscopy of CO on the well-ordered Ru(0001) surface, appearing at the turn of the millennium, used this method for obtaining Ru(0001) single-crystal surfaces.<sup>5</sup> A simpler method developed recently involved heating the Ru crystal in an H<sub>2</sub> stream;<sup>6</sup> it produced a well-ordered Ru(0001) surface as verified by Scanning Tunneling Microscopy (STM). This method shortened preparation time from days (UHV) to a few hours.<sup>7-9</sup> A modified method, subsequently reported further reduced the preparation time<sup>10</sup> in which crystals were inductively heated to 1700 K for 30-60 seconds in a stream of Ar-15% H<sub>2</sub>. STM pictures and voltammetry profiles on single-crystals thus obtained were essentially the same as those from the other two methods.

#### III. ELECTROCHEMISTRY OF SINGLE-CRYSTAL Ru SURFACES

#### 1. Voltammetry Characterization

Figure 2a displays the voltammetry curves of polycrystalline and Ru(0001) surfaces in 1 M H<sub>2</sub>SO<sub>4</sub>. The broad, featureless oxidationprocess at the polycrystalline electrode's surface involves currents about one order-of-magnitude larger than that of the single-crystal surface, and was attributed to the continuous oxidation of Ru in a process encompassing more than one electron per atom.<sup>11-13</sup> The potential regions of hydrogen adsorption and surface oxidation are generally acknowledged to almost overlap, since the Ru oxidation



Figure 2. Voltammetry curves for (a) polycrystalline Ru and Ru(0001) in 1 M  $H_2SO_4$ , and, (b) oxidation with different positive potential limits in 0.05 M  $H_2SO_4$ . Sweep rates: (a) 10 mV s<sup>-1</sup>, and (b) 20 mV s<sup>-1</sup>.

starts very early in the potential scale (0.2 V vs. RHE).<sup>†</sup> The electrochemical processes are more easily identified for electrode-posited Ru films<sup>11,14,15</sup> than for bulk metal.

Figure 2b shows the voltammetry curves for the surface oxidation of Ru(0001) in 0.05 M H<sub>2</sub>SO<sub>4</sub>. Similar curves are presented in several publications.<sup>5,9,16-18</sup> Before starting a sweep in the positive direction, the potential was held sufficiently long at the negative limit to ensure a negligible reduction current originating from the previous potential cycle. The voltammetry curves show a single anodic peak with a long tail extending to the onset of bulk oxidation, and two major cathodic peaks correlated to the reduction processes, which begin at 0.6 V. Surface oxidation occurs above 0.4 V, and the integrated anodic charge reaches levels required for an one-electron oxidation of the Ru(0001) surface (260  $\mu$ C cm<sup>-2</sup>) in the sweep up to 1 V. Increasing the sweep rate up to 500 mV s<sup>-1</sup> caused a linear increase in the current density, but repeated potential cycling between 0 and 1.2 V did not significantly change the voltammetry curves. These observations suggest that the oxidation of the Ru(0001) surface is limited to the top layer with one electron per atom exchange at the potential below the onset of bulk oxidation. This can be represented by the following reaction.

$$Ru-A^{-} + H_2O \rightarrow RuOH + H^{+} + e^{-} + A^{-}$$
 at  $E > 0.40V$  (1)

Several groups have published voltammetry studies of the Ru(0001) surface in solutions containing non-specifically adsorbed ions.<sup>5,8,9,16-28</sup> The voltammetric profile of the Ru(0001) surface in 0.1 M HClO<sub>4</sub> has an integrated charge between 0.1 and 1 V of 230  $\mu$ C cm<sup>-2</sup>, somewhat smaller than that required for an one-electron process, (dashed line in Fig. 3a).<sup>17</sup> A comparison of the processes in the two electrolytes indicates an effect of anion adsorption on the oxidation of the Ru surface. Strongly adsorbed bisulfate anions prevent OH adsorption due to water-oxidation at low potentials, and promote the complete removal of the oxygen-containing species in the cathodic sweep. Comparing the electrochemical processes with the opening of the anodic limit in the two acid

 $<sup>^{\</sup>dagger}\text{Unless}$  otherwise stated, all potentials are expressed vs. reversible hydrogen electrode, RHE.



Figure 3. Voltammetry curves for the Ru(0001) surface oxidation in (a) 0.1 M HClO<sub>4</sub> and (b) 0.1 M NaOH. Sweep rates: (a) 50 mV s<sup>-1</sup> and (b) 20 mV s<sup>-1</sup>. The inset in (a) shows the charge associated with the displacement of adsorbed species at 0.12 V by the adsorption of CO.

solutions suggests that the reduction process in perchloric acid solution cannot be completed without extending the sweep into the hydrogen adsorption/evolution region.<sup>17</sup> Indeed, extending the cathodic limit into the H<sub>2</sub> evolution region generates a large peak around -0.05 V (full line in Fig. 3a). The peak's associated charge is over 300  $\mu$ C cm<sup>-2</sup>, suggesting that it reflects a combination of at least two processes, one being hydrogen evolution. The other process, however, is puzzling. Since the same peak occurs in hydroxide solutions (see below), it is not due to perchlorate anion reduction. Also, it cannot be attributed to impurities in solution (like Cl<sup>-</sup>)<sup>28</sup> because it is not supported with adequate voltammetry response. The probable explanation is the reduction of adsorbed OH, as also suggested in a recent publication.<sup>29</sup> The subsequent positive sweep shows a much greater peak around 0.2 V, and another, smaller one around 0.4 V. A total charge of over 600 µC  $\text{cm}^{-2}$  is associated with the scan between -0.1 and 0.7 V.

To identify the nature of the species adsorbed at potentials from 0.1 to 0.25 V, a charge displacement technique was used, which was proven useful in identifying species on the Pt(111) electrode.<sup>30</sup> The electrode potential was held at 0.12 V and CO was introduced into the cell; there was no significant CO oxidation on Ru(0001). The charge associated with the resulting displacement process was negative, adding up to  $-117 \,\mu\text{C cm}^{-2}$  (see inset in Fig. 3a). If H<sub>ad</sub> was the adsorbed species in that potential region, the charge would be positive. Therefore, contrary the conclusions from other work,<sup>23</sup> the reaction must be associated with some oxygen-containing species. This finding was confirmed recently using the same approach.<sup>28</sup> A plausible reaction to account for this negative charge is

$$RuOH + CO_{soln} + e^{-} \rightarrow RuCO_{ad} + OH^{-}$$
(2)

The measurement at 0.25 V revealed again a negative charge, albeit a smaller one, of  $-31 \ \mu\text{C} \ \text{cm}^{-2}$  implying that some transformation took place in the species existing at 0.12 V. The difference between the charges at 0.12 and 0.25 V is 79  $\mu\text{C} \ \text{cm}^{-2}$ , in good agreement with 86  $\mu\text{C} \ \text{cm}^{-2}$ , the voltammetric charge in that potential interval. Interestingly, measurements in H<sub>2</sub>SO<sub>4</sub> solution do not show this process;<sup>17</sup> it is probably precluded by strong bisulfate adsorption on the hexagonal structure of Ru(0001). As discussed

later in this chapter, infrared spectroscopy and X-ray diffraction studies indicate that bisulfate adsorption on Ru(0001) is essentially at saturation coverage between 0.0 and 0.5 V, and that water chemisorbs on Ru(0001) in the absence of chemisorbed anions.<sup>16,17</sup>

Anion effects on the electrooxidation of Ru(0001) were explored by introducing Cl<sup>-</sup> and Br<sup>-</sup> into the 0.1 M HClO<sub>4</sub> solution.<sup>17</sup> A sharp rise of anodic current occurs near 0.2 V, which is at a more negative potential than the onset of surface oxidation in sulfuric acid. Hence, even though halide ions are strongly adsorbed, they do not better protect the Ru from surface oxidation than do bisulfate ions. It is likely that a different redox process occurs with halide ions because they form compounds with Ru in several different oxidation states.

Voltammetry of the oxidation of Ru(0001) in 0.1 M NaOH, Fig. 3b, shows a curve that has some similarities to that recorded in perchloric acid. The curve is dominated by a strong anodic peak at 0.25 V and a strong cathodic peak occurring at -0.05 V, the same potential as in perchloric acid. Its origin is not understood, as discussed. The multitude of peaks indicates the complexity of the oxidation/reduction processes. The symmetric peaks in this potential range on polycrystalline Ru were attributed to processes involving hydrogen adsorption and/or Ru oxidation.<sup>13,31,32</sup>

The voltammetry curve for the Ru( $10\overline{1}0$ ) surface in 0.05 M H<sub>2</sub>SO<sub>4</sub> solution (Fig. 4a) reveals a remarkable difference between the oxidation processes for Ru(0001) and Ru( $10\overline{1}0$ ). The oxidation of this face is more facile than that of Ru(0001), as indicated by the onset of the reaction at lower potentials and by increase of the charge with each potential cycle. This difference most likely is the consequence of the more open structure of the Ru( $10\overline{1}0$ ). A pair of peaks at 0.12 and 0.3 V is reminiscent of hydrogen adsorption on Pt metals. However, CO displacement showed a negative charge of  $-354 \ \mu C \ cm^{-2}$ . Thus, the peaks probably represent partial Ru oxidation to RuOH, wherein OH is the predominant adsorbed species, perhaps with some co-adsorption of bisulfate.

Unlike the behavior of the Ru(0001) surface, the gradual increase in the positive potential limit has deleterious effects on the ordering of Ru( $10\overline{1}0$ ). The increase of the charge associated with the voltammetry curve in each subsequent cycle indicates the oxi-



Figure 4. Voltammetry curves for the  $Ru(10\bar{1}0)$  surface in (a) 0.05 M H<sub>2</sub>SO<sub>4</sub> and (b) 0.1 M HCIO<sub>4</sub>. Sweep rates: (a) 20 mV s<sup>-1</sup> and (b) 50 mV s<sup>-1</sup>. The insert in (b) shows the charge associated with the peaks in the positive scan, obtained by peak fitting routine.

dation of several of the crystal's top atomic layers, similar to the behavior of polycrystalline Ru.<sup>11-13</sup>

Figure 4b shows the cyclic voltammetry of the Ru( $10\overline{1}0$ ) surface in 0.1 M HClO<sub>4</sub>. The voltammetry profile differs from that in sulfuric acid solution suggesting that sulfate absorption /desorption contributes to the peaks observed in Fig. 4a. The total charge in the positive sweep between 0 and 0.25 V is 247  $\mu$ C cm<sup>-2</sup>, which is greater than that required for an one-electron oxidation (159  $\mu$ C cm<sup>-2</sup>). The process that occurs between 0.05 and 0.3 V is probably associated with a large uptake of OH<sub>ad</sub>. Potential cycling to 0.8 V causes additional growth of oxide on this surface (cf. Fig. 4a), unlike the behavior of the Ru(0001) face. The striking differences between the two Ru single-crystal planes reveals the large stability of the hexagonal Ru(0001) surface and a pronounced reactivity of the rectangular Ru(1010) face.

#### 2. Surface X-Ray Diffraction Study

The electrochemical surface oxidation of Ru(0001) was characterized by *in situ* surface X-ray scattering techniques in acid solutions at potentials where the voltammetry curves show an one-electron surface oxidation process below the onset of bulk oxidation.<sup>17</sup> The analysis of the X-ray specular reflectivity found that the spacing between the top two Ru layers is 0.213 nm at 0.1 V, and 0.220 nm at 1.0 V in 1 M H<sub>2</sub>SO<sub>4</sub> solution, similar to those in the gas phase for bare Ru and for one monolayer (ML) of oxygen on Ru (0.210 and 0.222 nm, respectively). At low potentials, the specular reflectivity data support a model involving the co-adsorption of bisulfate and hydronium ions on Ru(0001). The coverage of bisulfate is close to 1/3 ML at potentials below 0.57 V. Figure 5 shows the proposed structural models. In contrast to the behavior of Pt(111) and Au(111) surfaces, no place exchange is involved in Ru(0001) surface oxidation. The formation of a monolayer of ruthenium



Figure 5. Proposed structural models for Ru(0001) oxidation, where the O, S, and Ru atoms are represented by the open, lightly-shaded, and heavily- shaded circles, respectively. The layer spacings are given in nm, and coverage is given in monolayers. Reprinted with permission from <sup>17</sup>. Copyright (2001) American Chemical Society.

oxide induces partial desorption of bisulfate, in agreement with the Fourier Transform infrared (FTIR) results (see Section III.3). Strikingly, oxygen penetration is completely blocked on Ru(0001) at potentials below the bulk oxidation potential, in contrast to the high degree of surface oxidation of polycrystalline Ru that occurs between the onset of hydrogen evolution to the onset of bulk oxidation. Since gas-phase studies demonstrated that subsurface oxygen plays a major role in the activity of Ru for CO oxidation, the lack of subsurface oxygen on the Ru(0001) electrode might explain its inactivity for CO electrooxidation; this interpretation is discussed below.

#### 3. Infrared Spectroscopy and Anion Adsorption

The adsorption of anions on solid surfaces is of considerable interest, mainly because of its effect on the kinetics of electrochemical reactions. Several *in-situ* techniques have been applied toward this purpose.<sup>33</sup> Infrared measurements were used to identify adsorbed species, estimate anion adsorption isotherms, and to gain information on anion interaction with electrode surfaces.<sup>34</sup> Sulfuric acid anions are possibly the commonest anion adsorbates because of their specific adsorption on metal surfaces. Depending on the metal, its surface orientation, and the concentration of anion, either sulfate or bisulfate can be specifically adsorbed on the surface. Identifying the predominant adsorbate on platinum-group metals has engendered some controversy. While STM studies show that sulfate and/or bisulfate on Pt metals of (111) orientation form a  $(\sqrt{3} \times \sqrt{7})$  overlayer,<sup>35</sup> questions remain about the nature of the species. Even though the symmetry differences of sulfate and bisulfate ions should, in principle, reveal the preferentially adsorbed species, the interpretation of the mostly equivalent *in situ* IR spectra may not be unique.<sup>36</sup> Two absorption bands around 1200 and 1100 cm<sup>-1</sup> observed on a polycrystalline Pt electrode were attributed to adsorbed bisulfate and sulfate, respectively.<sup>37</sup> In addition, a third band at 950 cm<sup>-1</sup> on polycrystalline Pt, led to the conclusion that both bisulfate and sulfate on the surface give rise to three bands.<sup>38</sup> For Pt (111), Nart et al. concluded that the adsorbate is sulfate coordinated via three oxygens presenting a  $C_{3v}$  symmetry,<sup>34</sup> while Faguy et al. argued that the adsorbed species is not described adequately as either sulfate or bisulfate but rather as an  $H_3O^+ - SO_4^{2-}$  ion pair.<sup>39</sup>

Recent data confirmed that the preferred species on Pt (111),<sup>40</sup> Pd<sup>41</sup> and Ir<sup>42</sup> is bisulfate, while sulfate adsorbs on Ag(111)<sup>43</sup> and on Au(111).<sup>44-46</sup> Apparently the *sd* metals (Rh, Pt, Pd) with (111) orientation adsorb bisulfate, whereas the *sp* metals (Cu, Ag, Au) adsorb sulfate. The IR study on Ru(0001) seemed to support this conclusion (see below), as the latter has the same orientation of surface atoms as the *fcc* metals of (111) orientation, and the adsorbed species is bisulfate.

#### (i) Polycrystalline Ru Electrode

As discussed in the previous Sections, electrochemical oxidation of polycrystalline Ru involves about one order-of-magnitude larger currents than that of Ru(0001), starting as early as 0.2 V.<sup>16</sup> Polycrystalline Ru is covered with hydroxyl ions from water very early in the potential scale even in acidic solutions, thus blocking the surface from anion adsorption by the supporting electrolyte. This conclusion is supported by the *in situ* IR spectra presented below.

Specific adsorption of sulfate-bisulfate generally displays spectral features that are blue shifted (i.e., to higher frequencies) with higher electrode potentials, as observed for both polycrystalline  $Pt^{37,38,47}$  and the Pt(111) surface.<sup>36</sup> The shift is explained in terms of one or more of the following mechanisms: electron donation between the adsorbate and the metal surface (vibronic coupling); coupling of the electric field that exists in the double layer with the dipole moment of the adsorbates (Stark effect); and, the interaction from dipole–dipole coupling due to an increase in coverage.<sup>48,49</sup> The absence of these mechanisms in the IR spectra shown in Fig. 6 for polycrystalline  $Ru-H_2SO_4$  system suggests that there is no specific adsorption of sulfuric acid anions.

Five distinctive potential-independent peaks are observed at 1100, 980, 1205, 1051, and 885 cm<sup>-1</sup> from the polycrystalline Ru surface in 0.05 M H<sub>2</sub>SO<sub>4</sub> (see Fig. 6a). The first two are associated with sulfate and the rest with the bisulfate species.<sup>50</sup> Positive-going bands in the  $-\Delta R/R$  representation show an increase of the species at the electrode's surface and/or in the solution layer sampled by the IR light at the sample's potential relative to that at the reference potential. However, adsorbed species at the electrode surface are sensitive only to the *p*-polarized light due to the surface-selection rule, while both polarizations interact equally with randomly oriented species in solution.<sup>51</sup> The fact that the intensity of both the sulfate and bisulfate bands rises with increasing electrode potential, and that their features are observed with both s- and p-polarized light, suggests strongly that the spectra represent solution species, i.e., the migration of ions into the diffuse part of the double layer to compensate for the charge buildup at the electrode surface. Therefore, a marked interaction of OH with polycrystalline Ru electrode at low potentials prevents sulfate-bisulfate adsorption throughout the whole potential region from hydrogen evolution to oxygen evolution.

#### (ii) Ru(0001) and $Ru(10\overline{1} 0)$ Single-Crystal Electrode Surfaces

Figure 6b shows a set of spectra taken at the Ru(0001) electrode in 0.05 M  $H_2SO_4$  solution. There is a well-defined bipolar peak with the positive lobe centered at 1280 cm<sup>-1</sup> that shifts with increasing potential. A similar band has been observed for several single crystal surfaces with hexagonal surface orientation.<sup>52</sup> On the basis of *ab initio* calculations for anion adsorption at the Pt(111) surface, Sawatari et al. concluded that the totally symmetric stretch of bisulfate at 1051 cm<sup>-1</sup> should undergo a large frequency shift.<sup>53</sup> In the IR spectrum given in the  $-\Delta R/R$  representation, this phenomenon should be visible as a positive-going, potential-



Figure 6. *In-situ* infrared spectra obtained from (a) polycrystalline Ru, and (b) Ru(0001) electrode in 0.05 M H<sub>2</sub>SO<sub>4</sub>. The reference spectrum is obtained at 0.03 V, and sample spectra are taken every 0.1 V, from 0.05 to 0.85 V. 4096 scans were co-added in 16 cycles, 256 scans each; the resolution was 8 cm<sup>-1</sup>. Spectra are offset for clarity. Reprinted from <sup>16</sup>, Copyright (2001) with permission from Elsevier.