

Electrochemical Reduction of Carbon Dioxide on Conductive Metallic Oxides

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showed a strong potential dependence which we postulate is due to a decrease in heterogeneous electron transfer rate at the polymer-gold interface. Calculations of the double layer correction indicate that electrostatic effects on the reaction plane potential are probably sufficient to produce the observed rate decreases.

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Electrochemical Reduction of Carbon Dioxide on Conductive Metallic Oxides

A. Bandi

Universität Stuttgart, Institut für Physikalische Elektronik, D 7000 Stuttgart 80, Germany

ABSTRACT

Faradaic efficiencies and current-voltage characteristics for the reduction of CO₂ on various conductive oxide mixtures (RuO₂, TiO₂, MoO₃, Co₃O₄, Rh₂O₃) were determined. Product analysis was performed by gas chromatography. Electrodes composed of RuO₂ + TiO₂ [35 + 65 mole percent (m/o)] and RuO₂ + Co₃O₄ + SnO₂ + TiO₂ (20 + 10 + 8 + 62 m/o) show high current efficiencies for methanol production when polarized near the equilibrium potential of hydrogen evolution in solutions of 0.2M Na₂SO₄ (pH = 4) saturated with CO₂. It can be concluded from the Tafel slopes that the first electron transfer is the rate-limiting step in the reduction of CO₂ on the investigated oxides in acidic media.

The electrochemical reduction of CO₂ to higher reduction products, like methanol or methane, is thermodynamically more favorable than water reduction ($E^\circ = 0.13\text{V}$, respectively, 0.2V vs. NHE). The reaction is, however, kinetically rather complex and needs effective electrocatalysts. In many studies made on metals with high overvoltage for hydrogen evolution, the main reaction products were CO or formic acid (1-3). Higher reduction products are obtained with semiconductors [e.g., (4-9)], with some metals having medium overvoltage for hydrogen evolution (10-13), or in homogeneous catalysis [e.g., (8, 14)].

Metallic conductive oxides like RuO₂, IrO₂, or Co₃O₄ have been known for several years to be very active catalysts in anodic processes like Cl₂, O₂ evolution, or in ca-

thodic reduction of O₂ (8, 15-19). In addition they possess high electrical conductivity (ca. $10^4 \Omega^{-1} \text{cm}^{-1}$) and electrochemical stability, especially when blended with other oxides. The high electrocatalytic activity of these oxides for O₂ evolution is correlated with the appropriate value of the chemisorption energy for an oxygenated species. This energy is itself a function of the enthalpy change for the lower-higher oxide transition ["volcano" curve (19)]. The electrochemical reduction of CO₂ to methanol occurs, probably, by dissociative chemisorption on metallic electrodes (20-22). Studies of the adsorption on oxides in the gas phase showed that in the presence of adsorbed hydrogen, CO₂ adsorbs by formation of carbonate, bicarbonate, formate, or metoxi adsorbates (21-30). Therefore, these oxides should be interesting catalysts for the reduction of

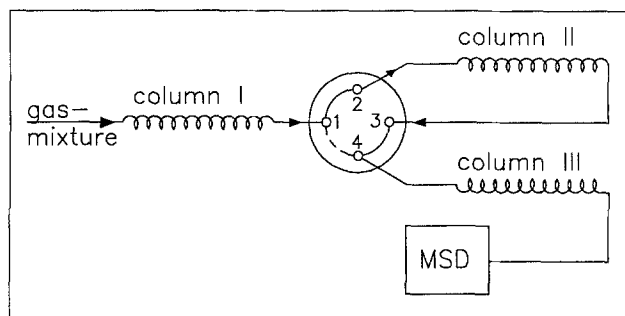


Fig. 1. Valve system and column sequence used in gas-phase analysis.

CO₂. In addition, the capacity of RuO₂ to adsorb hydrogen reversibly (31) may play an important role for CO₂ reduction. In this paper we report for the first time on the electrochemical reduction of CO₂ on mixed oxide electrodes with Ru, Mo, Co, Ti, and Sn as constituents.

Experimental

The oxide layers were prepared on titanium foil (Ventron M2N7 0.67 mm) using alcoholic and acidic solutions of the cations and subsequent thermal decomposition at 450°C in air. Typically 9-11 layers of solution were painted on the Ti substrate (1 cm² active surface). Each layer was annealed separately. The total amount of oxides deposited (≈ 4 mg/cm²) was determined by weighing the samples. The titanium substrate was etched in an oxalic acid solution (10%) before coating.

The electrochemical experiments were done in a two-compartment electrochemical cell (20-50 ml catholyte). The working electrode was pressed into a Teflon sample holder (PAR). Potentials were measured relative to a Hg₂SO₄ reference electrode. All solutions were prepared from reagent grade chemicals and bidistilled water. Before each run the solutions were deaerated with purified N₂ for 30 min (flow rate 10-11 liter/h) and then saturated with CO₂. The experiments were carried out in a closed system, CO₂ being recycled by a diaphragm gas pump (Romega 010). Both gases, CO₂ and N₂ (99.9993%) were washed in concentrated H₂SO₄ and then in H₂O. Polarization curves and cyclovoltammograms were recorded with a Heka potentiostat (PG/284) and BBC recorder (Type SE 780). Tafel plots were taken at a sweep rate of 1 mV/s, the cyclovoltammograms at 50 mV/s. The partial current of CO₂ reduction for Tafel representations was calculated from the current increase with respect to the measurement in N₂-saturated solution. It is hereby assumed that the current of hydrogen evolution is the same in both solutions. Longtime potentiostatic polarization was performed for product analysis. The pH of the solution was measured while being CO₂ saturated. All electrochemical experiments were done at 20°C.

Product analyses of the gas phase and of the solution were performed. CO₂ and distilled water were checked for impurities. The analyses were carried out with a Hewlett Packard GC-MSD system, HP-5890 and HP-5970B, moni-

tored by the workstation HP-59970C. A three-column system consisting of two packed columns (I and II) and a capillary column (III) were used (Fig. 1). This system allowed the separation of mixtures of fixed gases and organic components (32). The fixed gases were first eluted from column I, Poropak N, and passed through column II (1 $\rightarrow$ 2), molecular sieve 13 times, where they were separated. Then they passed through column III, HP-20M (Carbovac 20M, 25m $\times$ 0.2 mm) to enter in MSD. The last column served here as an interface from the packed columns to the MSD. Before organic compounds eluted from column I, a valve changed the gas flow to pass directly from column I in to column III (1 $\rightarrow$ 4), where they are separated. The products in the solution were analyzed by direct injection or headspace sample method with column III. The components were identified by their characteristic mass spectra and retention time information. The quantitative analysis was carried out with external standards prepared in the 5 $\times$ 10⁻¹ to 10² ppm concentration range. The concentration of the products was obtained by automatic integration of the peak area. The detection limit lies at 0.5 ppm for methanol and formic acid, 1 ppm for methane, carbon monoxide, and formaldehyde. In carbon dioxide no carbon monoxide, methane, or methanol could be identified. In distilled water 0.5 ppm methanol was found. The methanol concentration after CO₂ reduction was corrected by this amount. Both solution and gas analyses were carried out with temperature program. As carrier gas we used He (99.9993). The reproducibility of measurements was at about 90%. In the tables indicated concentrations are an average of about five measurements.

Results and Discussion

The various electrodes prepared are listed in Table I with the current efficiencies for methanol and formic acid production in 0.05M H₂SO₄ (pH = 1.2) polarized at -900 mV vs. Hg₂SO₄. Only methanol and formic acid were found in the solution. In the gas phase no reaction products were found. The current efficiencies were calculated from the total charge (Q_t) corresponding to the electrolysis current, and the charge involved in the reduction of CO₂ (Q_{red}), calculated from the amount of the product formed

$$\text{Efficiency [\%]} = \frac{Q_{\text{red}}}{Q_t} \times 100 \quad [1]$$

In Fig. 2 we present a typical chromatogram run [for analysis of electrode 1, see Table I] obtained in the "Selected Ion Monitoring" mode. Analysis of the water used for the preparation of the solutions is also shown in Fig. 2. Electrode 2 is of the same composition as 1 but with a trace of Ag (SIMS shows $\sim 1\%$ of Ag on the surface layer). The reaction product with electrode 2 is mainly HCOOH. The most efficient electrode composition for production of methanol at -900 mV vs. Hg₂SO₄ and pH = 1.2 is RuO₂ + TiO₂ (35 + 65 m/o), i.e., electrode 1, followed by electrodes 4 and 5. Hydrogen evolution was also evident on all electrodes.

Figure 3 shows a typical cyclovoltammogram for a RuO₂ + TiO₂ (35 + 65 m/o), electrode 1 in 0.05M H₂SO₄ (pH = 1.20),

Table I. Electrode composition and current efficiency for reduction of CO₂ on various oxide electrodes at -900 mV vs. Hg₂SO₄ in 0.05M H₂SO₄ (pH = 1.2)

Electrode composition [m/o]	Q [C]	i [mA/cm ²]	Product conc. [ppm]		Product eff. [%]	
			CH ₃ OH	HCOOH	CH ₃ OH	HCOOH
1. RuO ₂ + TiO ₂ 35 + 65	44.3	0.52	9.7	0.9	24	2
2. RuO ₂ + TiO ₂ 35 + 65 (Ag)	36.0	0.43	0.8	133.7	2	78
3. Rh ₂ O ₃ + TiO ₂ 20 + 80	30.0	0.91	3.5	—	5	—
4. RuO ₂ + MoO ₃ + TiO ₂ 25 + 30 + 45	31.0	0.51	10.2	<0.5	12	<1
5. RuO ₂ + Co ₃ O ₄ + SnO ₂ + TiO ₂ 20 + 10 + 8 + 62	34.5	0.54	6.7	59.2	7	18

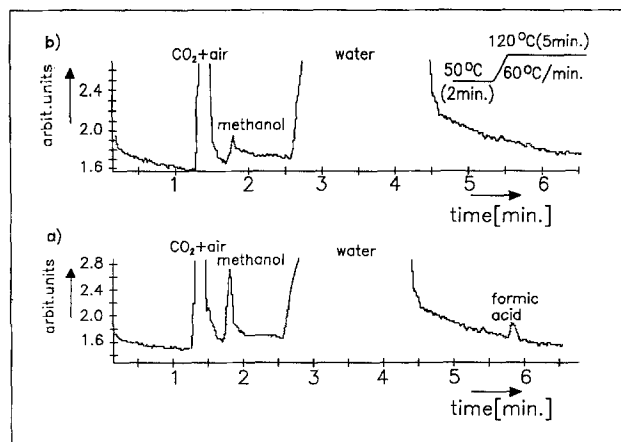


Fig. 2. Chromatograms obtained: (a) by analyzing of reduction products for electrode 1 (Table I), polarized at -900 mV vs. Hg_2SO_4 in 0.05M H_2SO_4 ($\text{pH} = 1.2$); (b) blank analysis for bidistilled water. The temperature program used is shown in the insert.

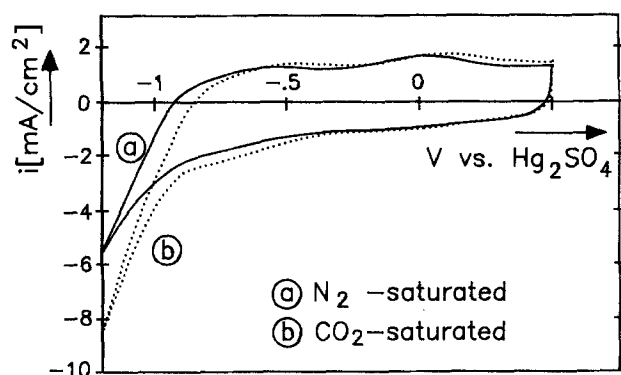


Fig. 3. Cyclic voltammograms for $\text{RuO}_2 + \text{TiO}_2$ (35 + 65 m/o) electrode 1 in 0.05M H_2SO_4 ($\text{pH} = 1.2$); potential sweep rate 50 mV/s.

saturated with N_2 and CO_2 , respectively. A higher current density is observed after saturation with CO_2 . An increase of the cathodic current was found by authors (4) when the solution was saturated with CO_2 on TiO_2 electrodes doped with RuO_2 in 0.5M KCl . They (4) concluded from the shape of the voltammograms that the reduction of CO_2 sets in before water reduction. As Tinnemans *et al.* (5) showed, the increase of the cathodic current in unbuffered solutions can be ascribed to the lowering the pH due to the saturation with CO_2 . However, the saturation with CO_2 cannot produce change of pH in 0.05M H_2SO_4 ($\text{pH} = 1.2$ before and after saturation) because carbonic acid is very weak in comparison with sulfuric acid.

The high buffer capacity of 0.05N H_2SO_4 prevents also a pH change on the electrode surface. Therefore, one can say that the higher current density observed in the solution saturated with CO_2 is due to CO_2 reduction. Figure 3 further shows that the reaction begins before the onset of water reduction. Therefore, we expect reduction products of CO_2 when the electrodes are polarized near the water re-

Table II. Current efficiency for reduction of CO_2 in solutions with various pH near the water reduction potential

Electrode	pH	Q [C]	i [mA/cm ²]	Product CH_3OH	
				Conc. [ppm]	Eff. [%]
1.	4.0 ^a	4.0	0.061	8.4	76
1.	6.0 ^b	5.2	0.077	5.0	35
1.	7.5 ^c	7.6	0.098	1.0	5
5.	4.0 ^a	4.7	0.052	6.8	53

^a 0.2M Na_2SO_4 .

^b Phosphate buffer (0.2M).

^c 0.5M KHCO_3 .

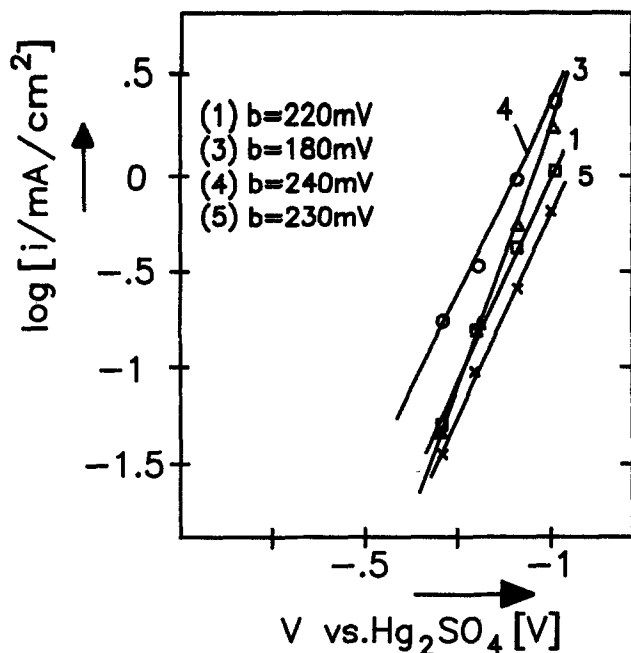


Fig. 4. Tafel plots of partial currents of CO_2 reduction in 0.05M H_2SO_4 ($\text{pH} = 1.2$) for electrodes 1, 3, 4, and 5.

duction potential. We present in Table II the current efficiencies for methanol for electrodes 1 and 5 (for composition see Table I), polarized near the water reduction potential in solutions with various pH. No other reaction products except methanol was found either in the solution or in the gas phase. There is a high current efficiency for methanol in solutions with pH of 4.0 for both electrodes and at pH = 6.0 for electrode 1. At these pH values we registered a pH change between the beginning and the end of polarization in the bulk of solution not greater than 0.2.

In order to determine the reaction mechanism, we recorded Tafel plots for CO_2 -reduction (partial currents) in 0.05M H_2SO_4 ($\text{pH} = 1.2$) for electrodes 1, 3, 4, and 5. The Tafel slopes for various oxide compositions (Fig. 4) lie between 180 – 240 mV. These details are similar to the ones found at higher current densities for the reduction of CO_2 on mercury (33) and other metals 1. The authors (33) associate this Tafel slope with the first electron transfer as rate-determining step. Several studies on oxides in the gas phase (22–26) showed that in presence of hydrogen the adsorption of CO_2 takes place by formation of carbonate, bicarbonate, formate, or metoxy adsorbates. Considering an

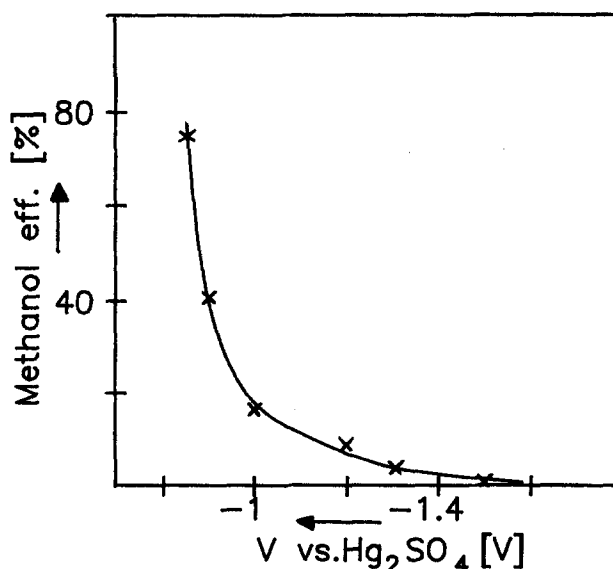


Fig. 5. The dependence of methanol efficiency on the polarization potential; electrode 1, 0.2M Na_2SO_4 ($\text{pH} = 4.0$).

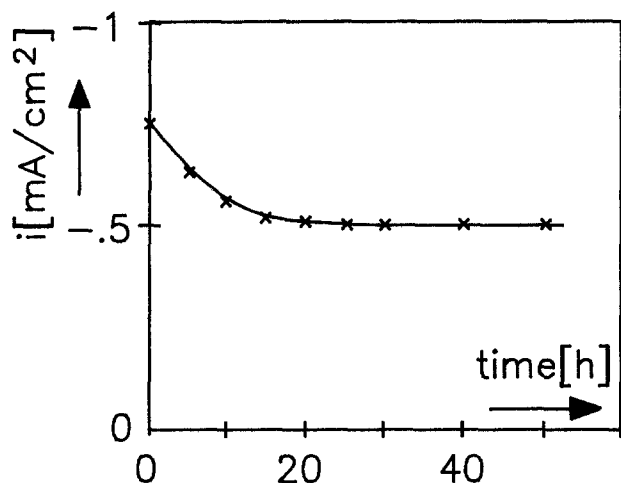
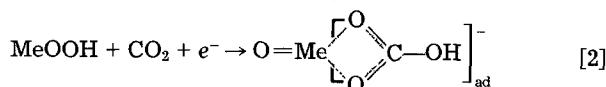


Fig. 6. Current-time plot for $\text{RuO}_2 + \text{TiO}_2$ (35 + 65 m/o) electrode in 0.05M H_2SO_4 (pH = 1.20) saturated with CO_2 at -900 mV vs. Hg_2SO_4 .

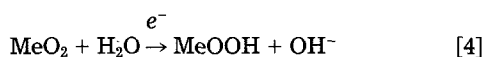
adsorption of CO_2 as bicarbonate on the hydrated oxide surface, the rate-determining step can be written as



with MeOOH being the result of the electrochemical hydration reaction of the surface. The electrochemical hydration can be considered as a partial reduction of the oxide surface. This reaction may be written for acid media as



and for neutral or basic media, depending of the acidity of the electrode



The dependence of methanol production efficiency upon the electrode potential was determined for electrode 1 in 0.2M Na_2SO_4 (pH = 4.0). The results are presented in Fig. 5. In this representation the total current is plotted. The efficiency falls strongly with increasingly negative potential, and at -1150 mV vs. Hg_2SO_4 the efficiency is <10%. We ascribe this pronounced decay in efficiency with potential to the increase of the rate of the hydrogen evolution reaction. The longtime polarization experiments show high stability for the oxide electrodes. In Fig. 6 is represented a typical i - t curve for electrode 1 in 0.05M H_2SO_4 (pH = 1.2), saturated with CO_2 . The current decays slightly in the first hours and then remains constant.

Summary

The metallic conductive oxide electrodes known as anodes for chlorine and oxygen evolution and other anodic processes show interesting catalytic properties for the electrochemical reduction of CO_2 . As reduction products, methanol and formic acid could be identified by gas chromatography. Mixtures of oxides of RuO_2 , TiO_2 , Co_3O_4 , MoO_2 , Rh_2O_3 , SnO_2 show a low overvoltage for the reduction of CO_2 . This reaction occurs before the onset of hydrogen evolution. At low current densities (≈ 50 -100 $\mu\text{A}/\text{cm}^2$), when the electrodes are polarized near the water reduction potential, there is a high current efficiency for methanol on mixtures of $\text{RuO}_2 + \text{TiO}_2$ (35 + 65 m/o) and $\text{RuO}_2 + \text{Co}_3\text{O}_4 + \text{SnO}_2 + \text{TiO}_2$ (20 + 10 + 8 + 62 m/o). For various oxides the Tafel slopes in 0.05M H_2SO_4 were found to be between 180 and 240 mV. In agreement with literature data (33), it seems that the first electron transfer is the rate-limiting step in the electrochemical reduction of CO_2 on oxide electrodes at pH = 1.2. The current efficiency for

methanol drops quickly with overpotential. Longtime polarization shows a good stability for the oxide electrodes. By changing the oxide composition and preparation parameters it might be possible to improve current densities and methanol efficiency.

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