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Reduction of chromate in dilute solution using hydrogen in a GBC-cell

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Reduction of metal ions in dilute solutions is of great interest for purification of waste waters and process liquids. Hydrogen gas is a very attractive reductant, since its use gives no additional pollution. In this paper the reduction of chromate in a sulphuric acid medium has been studied. A new electrochemical cell, a GBC-cell, which is a combination of a gas-diffusion electrode in direct contact with a packed bed of carbon particles, is introduced. Hydrogen gas flows along the hydrophobic side of the gas-diffusion electrode and a chromate solution is pumped upwards through the bed. Experiments were carried out with H_2SO_4 solutions initially containing 70 mol m^{-3} chromate at various temperatures, solution flow rates, H_2SO_4 concentrations and bed thicknesses. Experimental results for the chromate reduction are described by an empirical relation. It has been found that the reduction of chromate is a first-order reaction in chromate and the apparent rate constant for the chromate reduction increases with decreasing chromate concentration and increasing temperature, H_2SO_4 concentration and bed thicknesses and is practically independent of the flow rate of the solution. It is concluded that the new GBC-cell is very attractive for the reduction of chromate in dilute solutions and for industrial application on a large scale.

List of symbols

ϵ_b	void fraction of packed bed (dimensionless)	k	apparent rate constant of reaction (m s^{-1})
ρ_1	resistivity of solid phase of bed ($\Omega \text{ m}$)	k_C	k for reduction process with carbon (m s^{-1})
ρ_2	resistivity of liquid phase of bed ($\Omega \text{ m}$)	k_H	k for reduction process with hydrogen (m s^{-1})
a	empirical constant	k^0	apparent rate constant of reaction for an infinite c_b in chromate concentration (m s^{-1})
A_b	external surface area of carbon particles in packed bed (m^2)	k_{ov}	k for overall production process (m s^{-1})
a_C	a for reduction by carbon	L_b	thickness of packed bed (mm)
A_{bg}	cross section of packed bed (m^2)	n	number of electrons involved in electrode reaction (dimensionless)
A_{gd}	geometric surface area of gas diffusion electrode (m^2)	N	number of experiments in a series (dimensionless)
a_H	a for reduction by hydrogen	R	gas constant ($\text{J mol}^{-1} \text{ K}^{-1}$)
a_{ov}	a for overall process	t_s	time from the first sampling during the experiment (s or min)
b	empirical constant	T	temperature (K)
b_C	b for reduction by carbon	u_s	solution flow rate through the packed bed at the level of the gas diffusion electrode (m s^{-1})
b_H	b for reduction by hydrogen	U_s	volumetric solution flow rate ($\text{m}^3 \text{ s}^{-1}$)
b_{ov}	b for overall process	ν	rate of chromate reduction (mol s^{-1})
c_b	concentration of Cr^{6+} in bulk of solution (mol m^{-3})	ν_{ov}	ν for overall process (mol s^{-1})
$c_{b,i}$	c_b at inlet of bed-electrode compartment (mol m^{-3})	ν_C	ν for reduction with carbon (mol s^{-1})
$c_{b,o}$	c_b at outlet of bed-electrode compartment (mol m^{-3})	ν_H	ν for indirect reduction with hydrogen (mol s^{-1})
D	diffusion coefficient ($\text{m}^2 \text{ s}^{-1}$)	$\nu_{H,e}$	ν_H determined from current measured (mol s^{-1})
E	electrode potential vs SCE (V)	V_b	volume of carbon particles in packed bed (m^3)
E_C	equilibrium electrode potential vs SCE (V)	V_s	volume of cell solution (m^3)
F	Faraday constant ($96\,487 \text{ A s mol}^{-1}$)	X_c	fractional conversion of chromate (dimensionless)
ΔH_{act}	activation energy (kJ mol^{-1})		
I	current (A)		

1. Introduction

Reduction of metal ions in dilute solutions from e.g. plating and etching industries are carried out to minimize environmental problems. Three-dimensional electrodes, in particular packed bed electrodes, are very useful for the reduction of metal ions at very low concentrations, because of the large electrode specific surface area [1]. This type of electrode has been studied extensively during the previous twenty years [2]. Special attention has been paid to the removal of metals with packed bed electrodes in pilot plants or large-scale cells [3–6].

The packed bed cathode and, usually, two-dimensional anode, e.g. an expanded titanium grid or a nickel plate, are separated by a membrane or diaphragm. An external electrical power supply is used to deposit metal on the packed bed electrode from a solution containing metal ions. To reduce metal ions in a dilute solution, Janssen [7] has proposed an electrochemical reactor consisting of a hydrogen gas diffusion electrode in direct contact with a packed bed electrode, where two electrochemical processes, viz. reduction of metal ions at the carbon particles of the packed bed electrode and oxidation of hydrogen in the gas diffusion electrode, occur simultaneously and spontaneously. No external power supply is necessary to reduce, for instance, Cu^{2+} , CrO_4^{2-} and Fe^{3+} with hydrogen. In principle, any reduction process with hydrogen which can occur thermodynamically, can be carried out in the reactor mentioned.

Reduction of uranium (vi) in a concentrated solution [8] and, recently the reduction of hypochlorite [9] with a hydrogen gas diffusion electrode have been investigated. As far as is known, experimental results for a combination consisting of a gas diffusion electrode and a packed bed electrode have been published exclusively in [7]. Research on this combination of electrodes has been continued. In this paper results on the reduction of chromate by hydrogen are reported. Chromate reduction is considered as a model process and is of great interest for environmental reasons; chromate is formed in large quantities by anodic dissolution of stainless steel.

2. Experimental details

2.1. Experimental setup

The experimental setup consists of a gas diffusion electrode, a test cell, a solution storage vessel, a pump, a flowmeter and a heat exchanger. A schematic illustration of the experimental setup is given in [10].

The test cell is schematically represented in Fig. 1 and is called a GBC-cell, a Gas diffusion electrode-packed Bed electrode Cell. This cell is similar to that described in [10], except for the packed bed of carbon rods in the solution compartment of the cell. The cell has two compartments, viz. the gas compartment and the solution-bed compartment. The gas diffusion

Fig. 1. Schematic illustration of the GBC-cell. (1) Gas diffusion electrode, (2) gas compartment, (3) packed bed of carbon rods, (4) gas inlet, (5) gas outlet, (6) liquid inlet, (7) liquid outlet.

electrodes used were fuel cell grade electrodes on Toray paper (TGPH-120, E-Tek Inc., USA). A geometric surface area of 20 mm × 20 mm of the gas diffusion electrode was exposed to the solution and the packed bed. Some experiments were carried out with a polyvinyl cloth between the gas diffusion electrode and the packed bed to prevent direct contact between the two. In these experiments a platinum plate measuring 26 mm × 26 mm was placed against the rear of the packed bed. Moreover, the gas diffusion electrode and the platinum plate were connected externally and electrically via an ammeter.

The compartment of the cell through which the solution was pumped, was completely filled with the packed bed. The packed bed was constructed of small carbon rods 1 mm in diameter and about 3 mm in length (Norit RB1, type A-8009). The tapering part of the solution-bed compartment was 10 mm in thickness. The minimum bed thickness was 18 mm. The bed was made up of 5.20 g of carbon rods. Unless otherwise mentioned, experiments were carried out with the minimum bed thickness.

The bed thickness was enlarged by putting a square perspex body with a hole of 26 mm × 26 mm in between the cell part with the solution inlet and outlet and the back plate of the cell. 3.16 g of carbon rods was necessary to expand the bed thickness by 10 mm. Pure hydrogen gas was passed through the gas compartment of the cell. Some experiments were carried out with pure nitrogen fed to the gas diffusion electrode.

2.2. Solution, procedure and analysis

The solution was 350 cm³ H₂SO₄ containing a fixed concentration of K₂CrO₄, mostly 0.1 M. A flow meter (Fischer and Porter NV, tube 3F-3/8-25-G-5/36 with sapphire float) was used and calibrated. The

volumetric flow rate, U_s , was controlled. The flow rate is given by

$$u_s = \frac{U_s}{A_{bg} \epsilon_b} \quad (1)$$

The solution was circulated for about 25 min to reach the chosen temperature. Directly after adding the solution, nitrogen was passed through the gas compartment to remove oxygen gas from the gas diffusion electrode. After 15 min the nitrogen gas flow was replaced by a hydrogen gas flow. This procedure was applied to protect the gas diffusion electrode.

The first solution sample was taken about 10 min after starting the hydrogen gas flow. In this period the chromate concentration was decreased from 0.10 to about 0.070 M. A sample of 5 cm³ was taken after periods of about 10 min. The chromate concentration of the solution was determined iodometrically [11].

3. Results

3.1. Chromate reduction in a GBC-cell

Based on the potential-pH equilibrium diagram [12], it is assumed that Cr⁶⁺ is exclusively reduced to Cr³⁺.

3.1.1. Rate of chromate reduction. The chromate concentration in the solution was determined as a function of time, where pure hydrogen gas or pure nitrogen gas was used to feed the gas diffusion electrode. Typical results are given in Fig. 2 for 298 and 343 K. From Fig. 2 it follows that chromate is also reduced in the absence of hydrogen. Consequently, chromate also reacts with carbon from the packed bed.

To describe the complete reduction process in a GBC-cell the overall rate of chromate reduction is introduced and defined as follows:

$$-V_s \frac{dc_b}{dt} = \nu_{ov} = k_{ov} A_{gd} c_b \quad (2)$$

Taking into account the decrease in volume of cell solution during the experiment by sampling, the overall rate constant, k_{ov} , was obtained. Typical results are given in Fig. 3. These results were obtained from the

curves of Fig. 2, assuming k_{ov} is constant in the period between sampling. Moreover, k_{ov} is related to the average chromate concentration in the period considered. From Fig. 3 it follows that for nitrogen gas, k_{ov} does not depend on the chromate concentration, whereas for hydrogen gas, k_{ov} increases strongly with decreasing chromate concentration.

From these results it follows that k_{ov} for the reduction of chromate with carbon is independent of the chromate concentration, and for reduction with hydrogen it depends on the chromate concentration. In the latter case, k_{ov} is an apparent reaction rate constant.

To describe the reduction process in the GBC-cell, a practical correlation between k_{ov} and chromate concentration, c_b , is proposed. It has been found that the following correlation is appropriate:

$$k_{ov} = k_{ov}^0 + a_{ov} c_b^{-b_{ov}} \quad (3)$$

Using this correlation and taking into account the decrease in solution volume, the values of k_{ov}^0 , a_{ov} and b_{ov} were determined directly from the concentration/time curves.

3.1.2. Ageing effect of packed bed and gas diffusion electrode. To investigate the ageing effect, a series of experiments was carried out with the same carbon rods. In Fig. 4 k_{ov}^0 , a_{ov} and b_{ov} are plotted versus the experiment number. The series started with a packed bed of unused carbon rods, termed the fresh bed, and covered a period of about 2 months. Figure 4 shows the results for two supporting electrolytes, viz. 0.5 and 2.0 M H₂SO₄. During this series, experiments under different conditions were also carried out. From Fig. 4 it follows that k_{ov}^0 decreases and a_{ov} and b_{ov} increase with increasing N and these parameters depend on the sulphuric acid concentration.

After a series of 16 experiments (the results of a part of this series are given in Fig. 4) the packed bed of aged carbon rods was replaced by a bed of fresh carbon rods and the gas diffusion electrode was maintained. It was found that for a fresh bed the parameters k_{ov}^0 , a_{ov} and b_{ov} were the same before and after the series of 16 experiments with the same gas

Fig. 2. Chromate concentration, c_b , plotted against the time, t_s , after the first sampling for chromate reduction with a packed bed of aged particles in 1.0 M H₂SO₄ as the supporting electrolyte, at 298 K and using hydrogen (+) and nitrogen (♦) as the gas feed for the gas diffusion electrode and for a chromate reduction with a packed bed of fresh carbon particles in 0.5 M H₂SO₄ as supporting electrolyte, at 343 K and using hydrogen (▲) and nitrogen (■) as the gas feed for the gas diffusion electrode.

Fig. 3. Overall rate constant, k_{ov} , for the chromate reduction as a function of chromate concentration, c_b , for chromate reduction with a packed bed. Symbols as for Fig. 2.

diffusion electrode. Consequently, the change in the empirical parameters is caused by ageing of the carbon rods and not by a decrease in electrochemical activity of the platinum-loaded gas diffusion electrode.

3.1.3. Effect of solution flow rate. Preliminary experiments had shown that the effect of solution flow rate on the reduction rate was small. To eliminate the ageing effect of the packed bed, experiments with two strongly different rates of flow, 0.24 and 0.06 m s^{-1} , succeeded each other. The total series covered a period of 20 days. It was found that, for an aged bed, the empirical

parameters did not depend on the flow rate of the solution.

3.1.4. Effect of temperature. The series of experiments started with a fresh bed at the highest temperature and also ended at the highest temperature. Figure 5 shows the results. From this figure it follows that the bed was reasonably stable during these experiments. The parameter k_{ov}^0 increased and b_{ov} decreased with increasing temperature, whereas a_{ov} was almost independent of temperature.

3.1.5. Effect of bed thickness. The thickness of packed bed was varied as described in Section 2.1. Because of

Fig. 4. The empirical parameters, k_{ov}^0 , a_{ov} and b_{ov} as a function of the experiment number N in a series started with a bed of the same carbon rods for two H_2SO_4 concentrations, viz. 0.5 M ($\bullet$) and 2.0 M ($\square$). Other electrolysis conditions: temperature of 343 K , solution flow rate of 0.15 m s^{-1} , bed thickness of 18 mm and initial chromate concentration of 70 mol m^{-3} .

Fig. 5. The empirical parameters, k_{ov}^0 , a_{ov} and b_{ov} as a function of the temperature for a bed of fresh carbon rods. Other conditions: 0.5 M H_2SO_4 solution containing initially 70 mol m^{-3} chromate, solution flow rate of 0.15 m s^{-1} and bed thickness of 18 mm.

the construction of the cell, it is possible that the flow rate is not constant over the whole bed. The experiment with a bed thickness of 0 mm was an experiment without a bed. In this case, the solution flow rate was also 0.06 m s^{-1} . For various bed thicknesses, bed parameters and the experimental parameters k_{ov}^0 , a_{ov} and b_{ov} at 343 K are given in Table 1. Results are also given in Fig. 6. From this Figure it follows that k_{ov}^0 and a_{ov} increase linearly with increasing bed thickness and b_{ov} is practically constant.

3.2. Chromate reduction with carbon in and outside the GBC-cell

Experiments were carried out with the GBC-cell in which pure nitrogen was passed over the hydrophobic side of the gas diffusion electrode. Moreover, the reduction of chromate with carbon was also investigated outside the GBC-cell in separate experiments. In this case 2.5 g carbon particles were added to 200 cm^3 sulphuric acid solution containing $0.07 \text{ M CrO}_4^{2-}$. The solution with carbon particles was stirred with a magnetic stirrer and the solution was kept at the selected temperature. The chromate concentration was determined for various times after the

addition of the carbon particles. Assuming the internal surface of the carbon particles is of no interest for the chromate reduction, the rate of chromate reduction by carbon is given by

$$\nu_C = k_C A_b c_b \quad (4)$$

From the diameter, 1.0 mm, the length, 3.0 mm, and apparent density, 500 kg m^{-3} , the external surface area of carbon rods was calculated as $9.33 \text{ m}^2 \text{ kg}^{-1}$. Experiments were carried out with unused and used particles of carbon. It was found that the $\ln c_b$ against t curves between 5 to 120 min are linear. During the first period of 5 min a relatively much higher rate of chromate reduction occurs. Since,

$$\nu_C = -V_s \frac{dc_b}{dt} \quad (5)$$

it can be shown that the slope of the $\ln c_b$ against t curve is equal to $-k_C A_b / V_s$. From the linear part of the curve, the rate constant k_C for chromate reduction was calculated. It was found that k_C increases strongly with increasing sulphuric acid concentration, viz. k_C at 298 K and for 0.5, 1.0 and 2.0 M H_2SO_4 are 4.09×10^{-7} , 5.47×10^{-7} and $7.08 \times 10^{-7} \text{ m s}^{-1}$, respectively.

From experiments at various temperatures and assuming

$$k_{C,T} = k_{C,o} \left(\exp \left(-\frac{\Delta H_{act}}{RT} \right) \right) \quad (6)$$

it was established that ΔH_{act} is practically independent of the sulphuric acid concentration and its average value is 36.9 kJ mol^{-1} .

The effect of ageing of the carbon particles was also investigated. Three successive experiments were carried out for 2 h on one day with the same portion of carbon particles. It was found that k_C at 343 K and in 1.0 M H_2SO_4 for unused carbon particles and for the carbon particles used once and twice were 38.6×10^{-7} , 16.7×10^{-7} and $10.42 \times 10^{-7} \text{ m s}^{-1}$, respectively. This means that k_C depends strongly on the age of the carbon particles.

For the experiments with nitrogen gas $k_C = k_{ov} A_{gd} / A_b$. From A_{gd} / A_b for an 18 mm thick bed (Table 1), and from the results of Fig. 3 it was calculated that k_C for aged carbon particles at 298 K and for 1.0 M H_2SO_4 is $1.2 \times 10^{-7} \text{ m s}^{-1}$, and that k_C for unused carbon particles at 343 K and for 0.5 M H_2SO_4 is $12.2 \times 10^{-7} \text{ m s}^{-1}$. Comparing these values with those for unused carbon particles from the experiments in a stirred vessel, viz. $5.47 \times 10^{-7} \text{ m s}^{-1}$ at 298 K and $26.7 \times 10^{-7} \text{ m s}^{-1}$ at 343 K and taking into account the age of the carbon particles, it can be concluded that $k_C A_b / A_{gd}$ with the bed of carbon particles is smaller than $k_C A_b / A_{gd}$ with a stirred solution containing carbon particles.

In Table 1 k_C at 343 K is represented for a fresh bed of various thicknesses, L_b . The values for k_C for $L_b = 18$ and 66 mm were determined experimentally and those for 30 and 42 mm by linear interpolation.

Fig. 6. The empirical parameters, k_{ov}^0 , a_{ov} and b_{ov} as a function of bed thickness, L_b , for a GBC-cell with a bed of fresh carbon rods ($\circ$), without a bed ($\bullet$) and for a divided GBC-cell with a bed of fresh carbon rods ($\blacksquare$). Other conditions: 0.5 M H_2SO_4 solution containing initially 70 mol m^{-3} chromate, solution flow rate of 0.06 m s^{-1} and temperature of 343 K.

3.3. Chromate reduction in the GBC-cell with hydrogen

Assuming reduction of chromate with carbon and hydrogen are independent processes, then:

$$\nu_{ov} = \nu_C + \nu_H \quad (7)$$

The rate of chromate reduction with hydrogen is related to the rate of hydrogen oxidation. Three hydrogen molecules are used for the reduction of two molecules of chromate. The rate of chromate reduction with hydrogen is defined by

$$\nu_H = k_H A_{gd} c_b \quad (8)$$

Analogous to k_{ov} , the correlation between k_H and c_b is given by

$$k_H = k_H^0 + a_H c_b^{-b_H} \quad (9)$$

From the correlations for k_H and k_{ov} , and since k_C does not depend on the chromate concentration, it

can be shown that

$$k_H^0 = k_{ov}^0 - k_C \frac{A_b}{A_{gd}} \quad (10)$$

with $b_H = b_{ov}$ and $a_H = a_{ov}$.

Using these relations, the parameters for the indirect reduction of chromate with hydrogen can be obtained. The dependence of k_{ov} on the chromate concentration is then completely attributable to the indirect reduction of chromate with hydrogen.

For a fresh bed of various thicknesses, k_H^0 was calculated. Table 1 shows that k_H^0 increases with increasing bed thickness.

3.4. Divided GBC-cell

A GBC-cell was divided by positioning a diaphragm between the gas diffusion electrode and the packed bed of carbon particles. At the rear of the bed a

Table 1. Selected parameters for a fresh bed and the rate constants k_{ov}^0 , k_H^0 and $k_C A_b / A_{gd}$ for a GBC-cell with a fresh bed at various bed thicknesses L_b^*

L_b / mm	$10^3 A_b / \text{m}^2$	A_b / A_{gd}	$10^4 k_{ov}^0 / \text{m s}^{-1}$	$10^4 k_H^0 / \text{m s}^{-1}$	$10^4 k_C A_b / A_{gd} / \text{m s}^{-1}$
18	48.53	121	2.87	1.39	1.48
30	86.05	215	4.25	1.72	2.47
42	129.58	324	6.17	2.67	3.50
66	190.06	475	8.80	4.34	4.46

* For other conditions, see legend of Fig. 6.

Fig. 7. Overall rate of chromate reduction, ν_{ov} (■), rate of indirect chromate reduction by hydrogen, ν_H (+) determined by the usual method, and the one $\nu_{H,e}$ (◆) determined from current measurements as a function of chromate concentration, c_b , for a divided GBC-cell. Other conditions: 0.5 M H_2SO_4 solution containing initially 70 mol m^{-3} chromate, solution flow rate of 0.06 m s^{-1} and a temperature of 343 K.

platinum plate was placed. This plate covered the whole back side of the solution compartment of the cell and was connected externally with the gas diffusion electrode. The current was measured by an ammeter placed in the external circuit.

One experiment was carried out with a fresh bed in 0.5 M H_2SO_4 containing initially 70 mol m^{-3} chromate, at 343 K and a solution flow rate of 0.06 m s^{-1} .

The current, I , was converted to the rate of chromate reduction caused by hydrogen. It can be shown that

$$\nu_{H,e} = \frac{I}{nF} \quad (11)$$

where $n = 3$, corresponding to the three electrons used to reduce Cr^{6+} to Cr^{3+} .

The overall rate of chromate reduction, ν_{ov} , and the indirect rate of chromate reduction with hydrogen, viz. $\nu_H = \nu_{ov} - \nu_C$ were determined as described in Section 3.3. The rate of chromate reduction with carbon was calculated with $k_C = 12.2 \times 10^{-7} \text{ m s}^{-1}$ from Table 1.

In Figure 7 ν_{ov} , $\nu_{H,e}$ and ν_H are plotted versus the chromate concentration c_b . It follows that ν_H is clearly smaller than $\nu_{H,e}$. This result may be caused by additional reduction reactions in the packed bed consuming hydrogen, viz. possibly the reduction of oxygen dissolved in the cell solution during the experiment and the reduction of an oxide layer present on the carbon rods at the start of the experiment.

4. Discussion

4.1. Reduction of chromate by carbon

In the GBC-cell chromate in sulphuric acid medium is reduced to Cr^{3+} by hydrogen as well as carbon. This agrees with the standard potentials for the possible reactions [12]. From kinetic experiments (Section 3.2) it has been concluded that the reaction of chromate with carbon is a first order reaction in chromate. For the GBC-cell with an inert gas like nitrogen as feed for the gas diffusion electrode the calculated rate constant k_C for reduction of chromate by carbon (Fig. 3) is independent of the chromate concentration.

The rate constant k_C increases with increasing temperature and sulphuric acid concentration, but decreases strongly with increased ageing of the carbon particles. Moreover, it has been found that k_C for carbon particles in a stirred solution is clearly higher than that for carbon particles in a packed bed. This difference may be caused by a difference in crumbling between both types of experiments and channelling in the GBC-cell.

Because of the chromate concentration range used and the experimental rate of chromate reduction, the effect of flow rate is negligible.

The decrease in k_C with increasing ageing of the carbon particles (Section 3.2) also affects k_{ov} for chromate reduction in the GBC-cell with hydrogen gas. k_{ov} depends on the number of times, N , that a packed bed has been used. It was found that k_{ov}^0 and a_{ov} decrease and b_{ov} increases with increasing N (Fig. 4).

The activity of the gas diffusion electrode before and after the series of 16 experiments was not noticeably changed (Section 3.1.2). It is well-known that a platinum loaded gas diffusion electrode can be deactivated by oxidizing species [9]. It is likely that the change in the values of the parameters k_{ov}^0 , a_{ov} and b_{ov} at fixed conditions during the experiment with increasing N depends on many factors concerning the packed bed, for instance the time of the experiment, the waiting time between successive experiments, and the conditions during the periods when the GBC-cell was not used.

The ageing of the carbon particles is caused by oxidation of carbon by chromate and formation of sulphate or oxide compounds. An indication of the change in the nature of the carbon particles is that particles used for many experiments disintegrated into fine particles after drying in air.

4.2. Indirect reduction of chromate by hydrogen

Taking into account the contribution of k_C to k_{ov} , from Fig. 6 it follows that k_H^0 for a GBC-cell without a bed is much smaller than that for a GBC-cell with a bed. Moreover, taking into account $k_H^0 = k_{ov}^0 - k_C A_b / A_{gd}$, k_H^0 increases practically

linearly with increasing bed thickness. This means that the rate of chromate reduction related to hydrogen oxidation is practically uniformly distributed over the bed.

From experimental current/potential curves for a rotating glassy carbon electrode in a 1.0 M H_2SO_4 solution containing 20 mol m^{-3} chromate, it was found [14] that the limiting diffusion is obtained at the reversible hydrogen electrode potential for only rotation speeds lower than 4 r.p.s. and that the half-wave potential at a temperature of 298 K and a rotation speed of 4 r.p.s. is $+0.42 \text{ V}$ against the reversible hydrogen electrode. The latter result agrees with [5]. Assuming the kinetic parameters for chromate reduction on glassy carbon and carbon used in the bed are the same, and from the reversible normal potentials of the H_2/H^+ and $\text{Cr}^{6+}/\text{Cr}^{3+}$ couple, viz. 0 and 1.33 V, it follows that reduction in the GBC-cell takes place at a large electrode polarization. From the almost linear relation between k_{H}^0 and the bed thickness, L_{b} , it follows that the polarization over the whole bed in the GBC-cell is relatively large.

The results with the GBC-cell and the divided GBC-cell are comparable; k_{H}^0 for the divided GBC-cell is a factor of about 2.5 smaller than that for the GBC-cell (Fig. 6). This difference is almost entirely caused by the additional ohmic potential drop over the diaphragm in the divided GBC-cell. It was calculated that this ohmic potential drop decreases from about 0.36 to 0.15 V during the experiment. From this it follows, that the resistivity of the solid phase of the bed is much smaller than that of the liquid phase; the solid phase can be considered as a good conductor and $\rho_1 \approx 0$.

It can be shown that the chromate concentration at the outlet is negligibly smaller than that at the inlet of the GBC-cell and that the fractional conversion of chromate $X_{\text{c}} = (c_{\text{b,i}} - c_{\text{b,o}})/c_{\text{b,i}}$ defined according to [13] is practically zero. Consequently, the chromate concentration in the direction of solution flow is practically constant.

From Fig. 7 it can be deduced that k_{H} decreases with increasing chromate concentration. Moreover, k_{H}^0 is slightly influenced by the solution flow rate (Section 3.1.3), but strongly by the placing of a polyvinyl-cloth diaphragm in between the gas diffusion electrode and the bed of carbon particles (Fig. 6). Consequently, the diffusion of chromate is not rate-limiting for chromate reduction.

The other limiting case is the packed bed working under kinetic control [12]. In principle, the rate of chromate reduction in a GBC-cell decreases with increasing distance from the gas diffusion electrode. This decrease may be small and depends on many parameters, for instance, the ratio of the resistivities of the solid phase and the liquid phase of the packed bed, the thickness of packed bed, the exchange current density, the temperature and the specific surface area of the carbon rods [13].

The apparent rate constant k_{H} increases strongly with decreasing chromate concentration. The rate of

indirect chromate reduction by hydrogen, and thus the electric current through the liquid phase of the bed, increases with increasing chromate concentration. Due to the resistivity of the liquid phase of the bed, the distribution of current for indirect chromate reduction becomes less uniform with increasing chromate concentration, so that the efficiency of utilization of the bed, and the apparent rate constant k_{H} , decrease with increasing chromate concentration, c_{b} . Further research is planned to describe the relation between k_{H} and c_{b} , quantitatively.

If the packed bed is working completely under kinetic control, the almost linear relation between k_{H}^0 and L_{b} is contrary to the strong increase in k_{H} with decreasing c_{b} . It is likely that the diffusion of chromate to the carbon particles of the bed also affects the rate of chromate reduction, especially in the part of the bed near the gas diffusion electrode.

The effect of the H_2SO_4 concentration and temperature upon k_{H}^0 is very large (Fig. 4). The resistivity of the liquid phase of the bed, ρ_2 , decreases with increasing sulphuric acid concentration and temperature. Based on the results for chromate reduction by carbon it is likely that the apparent exchange current density of chromate reduction increases with increasing sulphuric acid concentration and temperature.

Consequently, it is difficult to estimate the effect of a higher sulphuric acid concentration and a higher temperature on the distribution of chromate reduction in the bed related to hydrogen oxidation.

To describe the current distribution in the bed quantitatively, more theoretical and experimental work will be carried out.

4.3. Application of a GBC-cell

It was found that a high rate of chromate reduction can be achieved in a GBC-cell with a hydrogen fed gas diffusion electrode. This cell has the advantages of packed bed cells, because of the high ratio between the geometric surface area of the packed bed and the geometric surface area of the gas diffusion electrode. The GBC-cell is attractive for redox processes which occur spontaneously and for which a high surface area is necessary, for instance, for electrode processes with a low exchange current density and to oxidize or reduce species in dilute solutions. A major advantage of the GBC-cell is the simple reactor design and the absence of an electrical circuit to regulate current or potential. This advantage may be of interest for special applications. It is also possible to use the concept of the divided GBC-cell. This concept may be useful for processes which do not occur spontaneously, for instance the removal of Pb^{2+} from dilute solutions with a hydrogen gas diffusion electrode. In this case, an external electrical energy source has to be used.

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