

INFLUENCE OF ELECTROLYTE HYDRODYNAMICS ON CURRENT YIELD IN FERRATE(VI) PRODUCTION BY ANODIC IRON DISSOLUTION

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Received July 15, 1999

Accepted November 18, 1999

The dependence of current efficiency for ferrate(VI) synthesis on the superimposed electrolyte flow rate was determined using 14 M NaOH solution and a white cast iron electrode. The electrolyte mean velocity in the cell ranged from 0.4 to 2.9 cm s⁻¹ and current density from 1.4 to 35.3 mA cm⁻². It was found that current efficiency was influenced by electrolyte velocity only at current densities lower than 7 mA cm⁻². This is explained in terms of the removal of intermediate products from the anode surface by the electrolyte convection. This factor becomes negligible at higher current densities in comparison to mass transfer induced by oxygen evolution on the anode surface.

Key words: Current efficiency; Mass transfer; Gas evolution; Iron oxidation; Ferrates; Electrochemistry.

A wide field of potential applications of ferrate (ferrate means ferrate(VI) throughout this text) is proposed in the literature. They are mainly based on his high redox potential, waste water treatment being most often referred to. Another possibility represents *e.g.* organic synthesis, corrosion protection or ore processing in the mining industry.

Studies of the influence of various parameters on the efficiency of electrochemical ferrate synthesis have been discussed in previous work¹⁻⁷. A key feature is the importance of the anode material composition and structure⁵. All these previous experiments were performed in a batch electrolytic cell under conditions of bubble-induced convection.

Another parameter influencing the efficiency of electrolysis, electrolyte hydrodynamics, was identified by Pick⁸. According to Pick, mixing of the electrolyte during electrolysis has a negative influence on the ferrate production current efficiency and in a limiting case it may stop it totally. The

influence of mixing is reduced by intensive cathodic prepolarisation of the iron anode and by long-term usage. A negative influence of electrolyte mixing on the ferrate yield was later confirmed by Toušek⁹. He observed that at a current density of 0.364 mA cm^{-2} , intensive electrolyte mixing suppressed ferrate production completely and practically only Fe(III) was found in the solution. At a higher current density of 54.2 mA cm^{-2} , no apparent influence of electrolyte mixing on ferrate yield was observed. Toušek explained this behaviour as being due to the necessity of the formation of a secondary passive layer on the anode surface necessary for successful ferrate production. At low current density and with electrolyte mixing (rotation rate of the mixer was kept constant throughout all Toušek's experiments) the anode material dissolves and no passive layer is built up. At higher current density oxide layer formation occurs and tends to minimise the influence of electrolyte mixing. Toušek did not carry out more detailed work on this phenomenon to support his suggestions.

The aim of the presented work is to assess more fully the effect of superimposed electrolyte convection on ferrate synthesis and to verify the hypothesis of Toušek⁹.

EXPERIMENTAL

The chemicals, analytical methods and apparatus were as used previously³. To assess the effect of flow, the cell was equipped with an external electrolyte circuit consisting of a peristaltic pump and silicone rubber tubing. The anolyte volume was 300 cm^3 . The composition of the white cast iron electrodes used is given in ref.⁴. Current yields were calculated with respect to the ferrate produced. The charge used for formation of oxides layer and iron in the lower oxidation states in the solution was not considered.

RESULTS AND DISCUSSION

The influence of the electrolyte hydrodynamics on ferrate yield was studied using white cast iron at $20 \text{ }^\circ\text{C}$ in 14 M NaOH , *i.e.* at conditions known to provide highest ferrate yields^{4,5}. The results are summarised in Fig. 1. It is clear that electrolyte-forced convection in the flow rate range up to 3 cm s^{-1} has no notable effect on the electrolysis results obtained at the two higher studied current densities. However, a decrease in ferrate concentration and current yield is observed for flow rates higher than approximately 1 cm s^{-1} at the two lower current densities, *i.e.* 1.4 and 1.8 mA cm^{-2} . To understand this behaviour it is necessary to discuss mass transfer phenomena. Mass transfer at the anode surface is controlled by both gas evolution and electrolyte-forced convection. For the case of mass transfer controlled by forced

convection, the mass transfer coefficient may be calculated using the following correlation¹⁰:

$$Sh = 0.023Re^{0.8} Sc^{1/3} \quad \text{for } Re > 2\,300 \quad (1a)$$

$$Sh = 1.85 \left(Re Sc \frac{d_e}{L} \right)^{1/3} \Phi \quad \text{for } Re < 2\,300, \quad (1b)$$

where Φ is a function of the relative dimensions of the cell.

No work dealing with a mass transfer to the oxygen-evolving iron electrode in such concentrated alkaline solutions, as used during the present study, is known to the authors. A review of mass transfer at gas-evolving electrodes was published by Vogt¹¹. Mass transfer at oxygen-evolving anodes in alkaline solutions was extensively studied by Janssen¹²⁻¹⁴. According to his results, the convection-penetration model is appropriate for oxygen-

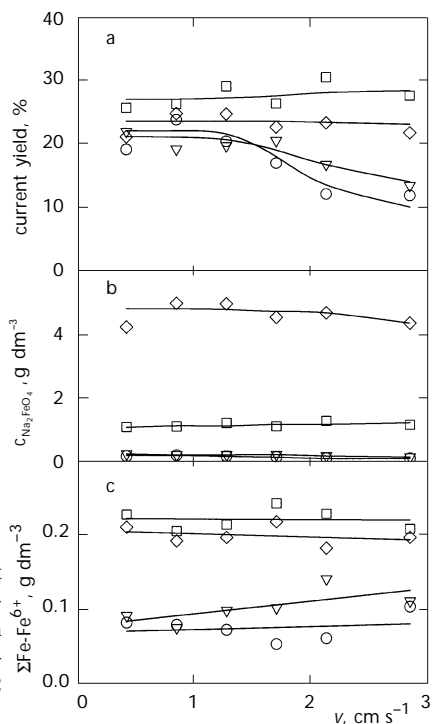


FIG. 1
Effect of flow rate variations on a current yield, b ferrate concentration and c concentration of iron in oxidation states lower than Fe^{6+} in solution of 14 M NaOH at 20 °C. Current densities ($mA\ cm^{-2}$): \circ 1.4, ∇ 1.8, \square 7.2 and \diamond 35.3

evolving electrodes. The equation for transfer of an indicator ion to an electrode was given as¹³:

$$k_g = \left(\frac{2a_d^2 A_d^2 D v_g d}{\pi V_d} \right)^{1/2} . \quad (2)$$

The value of the proportionality factor a_d was estimated as 1.7. The dependence of the average cross-section of detached bubbles, A_d , the volumetric production density of oxygen bubbles, v_g , and the volume of detached bubbles, V_d , on the current density were described by Eqs (3a)–(3c), respectively¹³.

$$A_d = 2.4 \cdot 10^{-9} j_o^{0.85} \quad (3a)$$

$$v_g = \eta_g 6.34 \cdot 10^{-5} j_o \quad (3b)$$

$$V_d = 1.2 \cdot 10^{-13} j_o^{1.21} \quad (3c)$$

Values of density of the sites from which bubbles depart, d , calculated in ref.¹³ on the base of experimentally determined mass-transfer coefficient values, were fitted using the least squares method by Eq. (3d).

$$d = 2.6 \cdot 10^8 j_o^{-0.33} \quad (3d)$$

The value of the current density j_o is in units of kA m^{-2} . The oxygen bubble formation efficiency, η_g , may be taken to be 0.5 (ref.¹³). All parameters were estimated in the presence of forced convection with $v = 0.12 \text{ m s}^{-1}$.

The diffusion coefficient of the key transferring species is in our case unknown. As suggested by Toušek⁹, the final electrolysis current yield is governed by the removal of an as yet unidentified intermediate product(s) from the electrode surface. A value for the diffusion coefficient of this species was arbitrarily set as $5 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$, a typical value for a soluble species in aqueous environment. Since the aim is to compare the contribution of two modes of mass transfer, each influenced by the diffusion coefficient in

a similar way, the error introduced in the comparison is less than 20% for the diffusion coefficient varying in the range $1 \cdot 10^{-10}$ to $1 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$. This is satisfactory in comparison to the accuracy of the description of the mass transfer to the oxygen-evolving electrode, which was developed for conditions dissimilar to those used in our work. The kinematic viscosity of 14 M NaOH at 20 °C is $2.54 \cdot 10^{-5} \text{ m}^2 \text{ s}^{-1}$ (ref.¹⁵).

For the evaluation of the combined mass transfer coefficient, k , Vogt¹⁶ has proposed the following relationship

$$k = \sqrt{k_f^2 + k_g^2} \quad (4)$$

Using the above relationships, the mass transfer coefficients corresponding to the two individual mass transfer mechanisms and the combined mass transfer coefficients were calculated for the individual studied electrolyte flow rates and current densities. The current density for oxygen evolution, j_o , was obtained from the total current density and the ferrate formation current efficiency obtained experimentally. Only two anode reactions were considered for the calculation, ferrate formation and oxygen evolution. The results obtained are summarised in Fig. 2.

It follows clearly from Fig. 2 that the combined mass transfer coefficient is significantly influenced by the superimposed electrolyte-forced convection only at the two lower current densities. Here the mass transfer coefficient increases by 50 and 45%, respectively, as electrolyte flow rate increases from 0.4 to 2.9 cm s^{-1} . This corresponds well to the decrease in

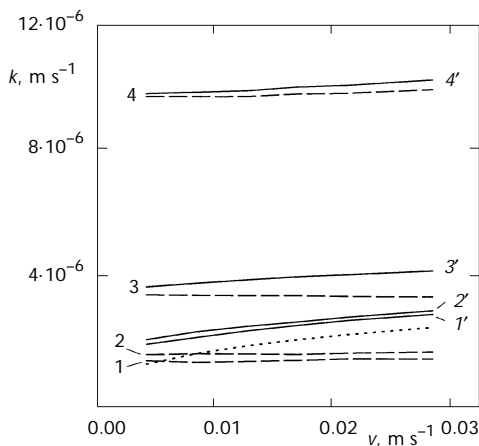


FIG. 2
Effect of electrolyte flow rate on calculated mass transfer coefficient in solution of 14 M NaOH at 20 °C. Dotted line, considering the electrolyte-forced convection only. Dashed lines, considering gas evolution without superimposed forced convection; current densities (mA cm^{-2}): 1 1.4, 2 1.8, 3 7.2 and 4 35.3. Full line, combined mass transfer coefficient; current densities (mA cm^{-2}): 1' 1.4, 2' 1.8, 3' 7.2 and 4' 35.3

the ferrate current yield by about 30 to 50% observed under the same conditions (see Fig. 1). On the other hand, at the two higher studied current densities, 7.2 and 35.3 mA cm⁻², the increase in mass transfer coefficient with electrolyte flow rate by 15 and 5%, respectively, falls practically within the experimental error of the current yield determination together with the error in mass transfer coefficient prediction. Correspondingly, as seen in Fig. 1a, at these conditions, the ferrate formation current yield shows no dependence on the electrolyte convection.

Two main conclusions follow from these results. Firstly, it is clear that anolyte flow rate is not an important design consideration for ferrate production using a cell with two-dimensional anodes. However, it may become an important parameter in the case of three-dimensional flow-through anodes, which are considered to be advantageous due to their high specific surface area¹⁷ and, consequently, very low real current densities.

Secondly, the negative influence of the mass transfer coefficient increase on the ferrate current yield is in a good agreement with previous theory suggesting at least one step in the ferrate formation mechanism proceeding in the homogeneous solution phase near the anode surface². If the soluble intermediate product is removed from the anode surface more rapidly, because of enhanced mass transfer, ferrate production current yield decreases, as stated previously by Toušek⁹. In the present case, mass transfer is controlled by both electrolyte convection and gas evolution on the anode surface. Therefore, electrolyte convection has an apparent influence on the ferrate current yield only at the two lowest current densities (1.4 and 1.8 mA cm⁻²), where its influence on the combined mass transfer coefficient is comparable with that of the oxygen evolution.

In seeming contradiction to this theory is the dependence of ferrate current yield on the current density. Even for a strong increase in mass transfer coefficient with increasing current density, caused by more intensive oxygen evolution, the current yield at higher current densities (7.2 and 35.3 mA cm⁻²) remains practically constant or even increases slightly in comparison to the lower current density range (see Fig. 1a). This is caused by saturation of the bulk electrolyte with iron in lower oxidation states as shown in Fig. 1c. Under this condition, transport of intermediate products from the anode surface is reduced and their further oxidation to ferrate is enhanced. This offers a more realistic explanation of the current yield being independent of electrolyte hydrodynamics at higher current densities than that given by Toušek⁹. Toušek's proposal of precipitation of the intermediate oxidation products on the anode surface would more probably result in

an anode deactivation and not in an enhancement of the ferrate production.

CONCLUSION

It was found that increase in the mass transfer coefficient at the anode surface results in a decrease in ferrate current yield. This is connected with the previously proposed ferrate formation mechanism² considering at least one step to proceed in the homogeneous phase near the anode surface. Oxygen evolution on the anode surface was identified as a key phenomenon influencing the mass transfer coefficient. Superimposed electrolyte-forced convection plays an important role only in limiting cases of very low current densities. However, in the case of three-dimensional anodes, where true current density is very low, superficial anolyte velocity may become an important parameter.

SYMBOLS

a_d	proportionality factor
A_d	average cross-section of detached bubble, m^2
d	density of bubble departure sites, m^{-2}
d_e	equivalent diameter of cell $d_e = 4S/P$, m
D	diffusion coefficient, $m^2 s^{-1}$
j_o	oxygen evolution current density, $kA m^{-2}$
k	combined mass transfer coefficient, $m s^{-1}$
k_t	mass transfer coefficient for electrolyte forced convection without gas evolution at the electrode surface, $m s^{-1}$
k_g	mass transfer coefficient for gas evolving electrode without electrolyte forced convection, $m s^{-1}$
L	active electrode length, m
P	wetted perimeter of flow channel, m
S	cross-section area of flow channel, m^2
v_g	volumetric gas bubble production per unit area, $m s^{-1}$
v_e	electrolyte superficial flow velocity, $m s^{-1}$
V_d	average volume of detached bubble, m^3
μ_e	electrolyte kinematic viscosity, $m^2 s^{-1}$
η_g	efficiency of oxygen bubble formation
Φ	correction function, Eq. (1b)

Dimensionless numbers

Re	Reynolds number $Re = d_e v_e / \mu_e$
Sc	Schmidt number $Sc = \mu_e / D$
Sh	Sherwood number $Sh = k_t d_e / D$

Financial support of this work by the Grant Agency of the Czech Republic (grant No. 104/99/0433) is gratefully acknowledged.

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