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SHORT COMMUNICATION

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A note regarding the rate-determining step of reduction of solid manganates(V)

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Abstract Potential pulse chonoamperometry was applied to immobilized microparticles of manganates(V) and MnO_2 in order to compare the nature of the rate determining step in their reduction. Manganates(V) were found to be reduced by an irreversible one-electron surface reaction, whereas MnO_2 reduction is controlled by a reversible reaction coupled to solid-state diffusion. The key importance of the coordination preferences of reacting metal ions on the surface layer of the solid particles is also discussed with respect to known mechanisms of electrochemical dissolution of Fe and Cr oxides.

Key words Electrochemistry · Manganates(V) · Mn oxides

The electrochemical reactions of metal oxides are very important and widely studied processes. These reactions are also investigated by voltammetry using carbon-paste electroactive electrodes or abrasive stripping voltammetry. The main goal of the theoretical treatment of voltammetric data traditionally involves qualitative and quantitative analysis, comparison of various solids, and modeling. Nevertheless, data interpretation is a far from simple task owing to the general complexity of heterogeneous reaction kinetics and the particulate nature of the reactant.

There are several possible pathways for the electrochemical reactions of solids. One of the possible mechanisms is preliminary dissolution of the solid reactant followed by an electrochemical reaction of the soluble species. This case was modeled for V_2O_5 reduction on carbon paste electrodes [1] and preliminary dissolution is also expected for reduction of Mn(III) oxides in alkaline solution [2], but this mechanism is rather exceptional for other transition metal oxides. Let us therefore consider the case where the redox reaction proceeds directly on the hydrated surface of the oxide, i.e., on the sites that are denoted by $\{\equiv \mathrm{Me}^m\}$. The primary reaction product is hence a surface metal ion with a changed valence but remaining in the lattice, $\{\equiv \mathrm{Me}^n\}$, where $m \neq n$. If $\{\equiv \mathrm{Me}^n\}$ is unstable in the original crystal lattice, the solid phase decays. The result can be dissolution (ferric and chromic oxides [3]), ion incorporation via a topochemical reaction (conversion of MnO_2 to MnOOH [2], $Sr_2Co_2O_5$ to $SrCoO_3$ [4]), or formation of a new solid phase via a heterogeneous reaction ($Mn(OH)_2$ formed from MnOOH via dissolution-reprecipitation mechanism in strongly alkaline solution [2], TiO_2 gradually covering dissolved $CaTiO_3$ [3]). The rate of the consumption of the reactant depends on thermodynamic and kinetic factors; it is probable that when the coordination number of $\{\equiv \mathrm{Me}^n\}$ differs from that of $\{\equiv \mathrm{Me}^m\}$, the further decay of the solid will be very fast and independent of potential; otherwise the dissolution could proceed via a normal chemical reaction of $\{\equiv \mathrm{Me}^n\}$with the solution.

Cr and Fe oxides could be given as two well-known examples of the dissolution reaction of metal oxides [3]. Ferric oxides are relatively quickly dissolved after surface reduction of $\{\equiv \mathrm{Fe}^{\mathrm{III}}\}$ to $\{\equiv \mathrm{Fe}^{\mathrm{II}}\}$ followed by formation and detachment of soluble ferrous ions, Fe^{2+}(aq). The first step proceeds on the hydrated surface layer of the oxides:

$$\{\equiv \mathrm{Fe}^{\mathrm{III}}\} + e^- \xleftrightarrow{\mathrm{H}^+} \{\equiv \mathrm{Fe}^{\mathrm{II}}\} \quad (1)$$

The subsequent step is rate-determining:

$$\{\equiv \mathrm{Fe}^{\mathrm{II}}\} \xleftrightarrow{\mathrm{H}^+} \mathrm{Fe}^{2+}(\mathrm{aq}) \quad (2)$$

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where Fe^{2+}(aq) denotes a soluble ion freely diffusing to the solution. The results of voltammetric dissolution of immobilized ferric oxides are consistent with Eqs. 1 and 2 [5, 6].

On the other hand, Cr^{III} oxides are dissolved by a sequence of two one-electron reactions (at least in the presence of one-electron oxidants) [7–9]. The process starts by

$$\{\equiv Cr^{III}\}_O \longleftrightarrow \{\equiv Cr^{IV}\}_O + e^- \tag{3}$$

where the subscript O denotes octahedrally coordinated Cr species. Because Cr^{4+} is not soluble in aqueous solution and is relatively stable in the octahedral environment within the original crystal lattice, the reaction described by Eq. 3 is followed by a subsequent oxidation on the surface of the solid that is likely accompanied by spontaneous rearrangement of the coordination sphere of {≡Cr}, because Cr^{5+} is no longer stable in the octahedral site in the original crystal lattice:

$$\{\equiv Cr^{IV}\}_O \xrightarrow{-e^-} \{\equiv Cr^{V}\}_O \xrightarrow{\text{fast}} [Cr^{V}]_T \tag{4}$$

The subscript T denotes a tetrahedrally coordinated Cr species, and square brackets denote an unknown structure of the intermediate. This step hence means the destruction of the crystal lattice of the oxide in the surface layer. Also during chemical oxidation of the dissolved ions Cr^{3+}(aq), the step between the Cr(IV) and Cr(V) intermediates accompanied by the change in the coordination sphere is the rate-determining step [10]. The oxidative dissolution of the solid is completed by the formation of easily soluble and thermodynamically stable chromate:

$$[Cr^{V}]_T \xrightarrow{\text{fast}} CrO_4^{2-} \tag{5}$$

This reaction scheme is also consistent with the electrochemical dissolution of chromic oxides [11]. To have a full picture, we must mention that chemical dissolution of chromic oxides by the action of oxo salts is triggered by oxygen transfer, $\{\equiv Cr^{III}\} \xrightarrow{O} \{\equiv Cr^{V}\}$, i.e., via direct two-electron oxidation [3, 12].

Recently, electrochemical reductive breakdown of manganates(V) was described and the corresponding voltammetric peak potential was reported to be proportional to the Mn-O distance in the crystal lattice [13], which intimates that the breakdown rate is determined by some simple reaction. Let us apply the general considerations described above to the reaction of manganates in order to find the possible rate-determining step.

Mn^{V} salts contain tetrahedrally coordinated Mn ions. Because Mn^{IV} ions prefer octahedral coordination, Mn^{V} reduction should be accompanied by abrupt rearrangement of the coordination surroundings of the Mn ions. We can suppose that this step triggers the solid phase decay in a way resembling the reaction of Cr oxides according to Eq. 4. As has been pointed out [13], solid particles of Mn^{V} salts are reduced at more negative potentials than Mn^{IV} and Mn^{III} oxides. With respect to the above-given considerations, the following general scheme should hence be expected for reductive dissolution of Mn^{V} oxides.

The first one-electron step yields Mn^{IV} which cannot exist in the original lattice owing to structural reasons:

$$\{\equiv Mn^{V}\}_T + e^- \longrightarrow \{\equiv Mn^{IV}\}_T \longrightarrow [Mn^{IV}]_O \tag{6}$$

Note that Eq. 6 resembles Eq. 4. Owing to the large overpotential needed for the electrochemical reaction, Mn^{IV} is immediately further reduced:

$$Mn^{IV} + e^- \xrightarrow{\text{fast}} Mn^{III} \tag{7}$$

that is followed by either

$$Mn^{III} + e^- \xrightarrow{\text{fast}} Mn^{2+}(aq) \tag{8}$$

or by precipitation of some secondary solid phase of Mn^{IV} to Mn^{II}.

Two samples of manganates(V), namely LT-$Ba_3(MnO_4)_2$ and $Sr_5(MnO_4)_3OH$, and MnO_2 were studied using the method of potential pulse chronoamperometry (PPC) [6] in order to characterize the rate-determining step. The samples of manganates(V) have been described elsewhere [13]. MnO_2 was obtained by boiling a suspension of Mn_3O_4 in HNO_3. The PPC method is based on chronoamperometry with repeated 20 s pulses (amplitude −10 mV). The electrochemical measurements were performed in a stream of N_2 in 9 M KOH saturated with $Ba(OH)_2$. A Pt plate electrode was used as the working electrode as described previously [13, 14], and their potential was measured versus a saturated calomel reference electrode. A μAutolab potentiostat (Eco Chemie, Utrecht, The Netherlands) was used for performing the electrochemical measurements.

Linear sweep voltammetric curves of particulate manganates(V) and MnO_2 were similar to those obtained by Fiedler et al. [13] and Fiedler [14], respectively. The PPC curves of the studied manganates were obtained at three potentials in the rising part of the voltammetric peaks. The principle of PPC and examples of the experimental data are shown in Fig. 1. The method is based on the assumption that the current corresponding to heterogeneous reactions of powders can be expressed as follows:

$$I = Q_0 k(E) f(y) \tag{9}$$

where Q_0 is a total charge corresponding to the reaction $Q_0 = \int_0^\infty I dt$, $k(E)$ is a rate coefficient, and $f(y)$ is a kinetic function of reaction extent y. Equation 9 is adapted from the kinetic equations for the thermal reaction of powders [15] and its purpose is to separate the influence of intensive variables (here the electrochemical potential) from the particulate character of the reactant. For irreversible electrochemical reactions with m totally exchanged electrons per metal ion proceeding at E_B, Eq. 9 changes to

$$I_B = mFN_0 k_0 \exp(AE_B) f(y) \tag{10}$$

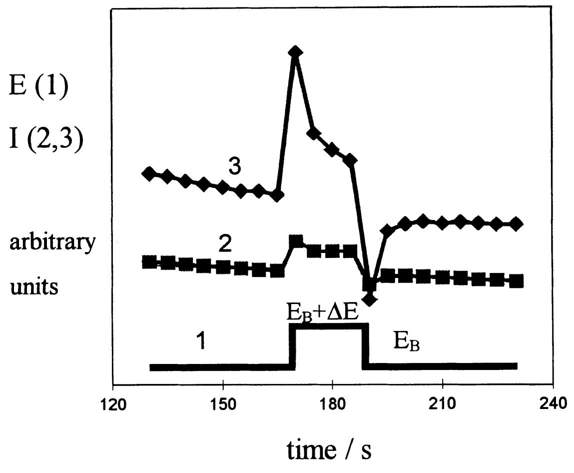

Fig. 1 Scheme of the potential pulse (*1*) and the resulting current responses of an irreversible surface reaction (*2*) and for a reversible ion insertion (*3*). *Curve 1* Potential pulse △ applied on basic potential E_B; *curve 2* reductive decay of $Sr_5(MnO_4)_3OH$ ($E_B = -0.53$ V); *curve3*: intercalation of H^+ into MnO_2 ($E_B = -0.33$ V)

where F is the Faraday constant, N_0 is the total molar amount of reactant, $A = \alpha nF/RT$ is the formal charge-transfer coefficient, n is the number of electrons relevant to the rate-determining step, and k_0 is the rate coefficient at the potential of the reference electrode; $n = 1$ for a one-electron reaction preceding the chemical rate-determining step (like reductive dissolution of ferric oxides with $A \approx 25$ [5, 6]), and $n = 2$ for a one-electron reaction followed by one-electron rate-determining step (oxidative dissolution of Cr oxides, $A \approx 50\ V^{-1}$ [11]). Note that $m \geq n$. Application of a sudden change of potential by ΔE volts causes the change of I_B to $I_{B+\Delta}$:

$$I_{B+\Delta} = Q_0 k_0 \exp(aE_B) \exp(A \cdot \Delta E) f(y) \qquad (11)$$

A may be obtained from Eq. 10 when a correction on changing $f(y)$ is done:

$$\ln(I_{B+\Delta}) - \ln(I_B) = A \cdot \Delta E \qquad (12)$$

The pulse should be rather short to minimize the change of $f(y)$. When the reaction rate is controlled by a surface reaction, the current course after having applied the potential pulse resembles that at the base potential E_B, and the extrapolation of $I(t)$ during the potential pulse (see curve 2 in Fig. 1) is easy (for fitting the kinetic curves of the surface reaction, see [5, 6, 9, 11, 16]). Both studied manganates(V) followed the kinetics of a surface reaction.

On the other hand, when the reaction is a reversible process controlled by solid-state diffusion (incorporation of ions), sudden changes of potential disturb the steady-state diffusion flux and so the current response changes markedly after the potential changes (see curve 3 in Fig. 1). In the latter case, Eq. 10 is not applicable.

The observed current response of the particulate manganates(V) to −10 mV pulses corresponds to a formal charge-transfer coefficient $A \approx 32$ according to eq. 10 (see Table 1 for results). Such a value of A can be related either to one-electron reduction with $\alpha = 0.8$, or to two-electron reaction with an average value of the individual steps of $\alpha = 0.4$. With respect to known formal charge-transfer coefficients of electrochemical dissolution of particulate ferric and chromic oxides ($\alpha > 0.5$ [5, 6, 9, 11]), $n = 1$ is more probable. Unlike electrochemical dissolution of Fe and Cr oxides, A for manganates(V) does not change with changing potential E_B, which indicates that there is no electrochemical equilibrium preceding the rate-determining step. A is almost independent of the reaction extent y, $y = \int_0^t I\,dt/Q_0$ (see Table 1), which shows that the reaction is not limited by diffusion through a compact layer of solid product in the later stages.

These results clearly indicate that the labilization of Mn ions in the original crystal lattice by reducing Mn(V) to Mn(IV) according to Eq. 6 is the rate-determining step. The hypothesis of a single rate-determining step is also supported by the surprising direct relation between peak potential and Mn-O distance in the oxide lattice [13]. The following rate-determining step (one electron per Mn ion) can hence be proposed, e.g., for strontium manganate(V):

$$Sr_5(MnO_4)_3OH + 3e^- + 6H_2O \xrightarrow{\text{slow}} 3MnO_2(s) + 5Sr^{2+}(aq) + 13OH^-$$

The new solid phase, MnO_2, or the subsequently formed solid products arise either as a porous cover of the reactant or are accumulated beside the reactant particles, enabling a complete conversion of the manganates(V) without changing the rate-determining step.

Table 1 Formal charge-transfer coefficients of reductive breakdown of manganates(V) obtained by potential pulse chronoamperometry.

	E_B, V	A		
		$0.2 < y < 0.3$	$0.4 < y < 0.5$	$0.6 < y < 0.7$
LT–$Ba_3(MnO_4)_2$	−0.49	29	27	27
	−0.53	32	32	31
	−0.56	34	27	26
$Sr_5(MnO_4)_3OH$	−0.49	32	30	32
	−0.53	34	33	33
	−0.56	31	31	31

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