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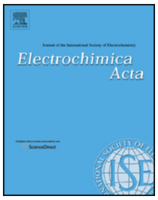

Electroreduction of halogen oxoanions via autocatalytic redox mediation by halide anions: novel EC” mechanism. Theory for stationary 1D regime

Mikhail A. Vorotyntsev[a,b,c,d,*], Dmitry V. Konev[a,d], Yuriy V. Tolmachev[e,*]

[a] Institute for Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Russia
[b] ICMUB, UMR 6302 CNRS-Université de Bourgogne, Dijon, France
[c] M.V. Lomonosov Moscow State University, Moscow, Russia
[d] D.I. Mendeleev Russian University of Chemical Technology University, Moscow, Russia
[e] Ftorion, Inc., Boston, MA 02120, USA

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ABSTRACT

Theoretical analysis of the system with coupled electrochemical and chemical steps has been carried out where bulk solution contains non-electroactive halogen oxoanions, XO_n^-, with a very small addition of halogen molecules, X_2. The latter are electroreduced rapidly at the electrode surface, generating halide anions, X^-, which diffuse towards solution, wherein they comproportionate with the principal oxidant, XO_n^-, yielding electroactive halogen. Unlike the well-known catalytic EC’ mechanism where both the electrochemical reaction and the chemical step retain the total amount of the mediating redox couple, the passage of the electroreduction cycle in the system under our study results in an increase of the total content of its components, halogen and halide anion, via the consumption of halate anions. We propose to denote this new autocatalytic EC mechanism as EC”. Approximate analytical formulas have been derived for all characteristics of this system under steady state conditions at the uniformly accessible electrode surface. We found that the behavior of the system depends crucially on the relation between the diffusion layer thickness, z_d, and the kinetic layer thickness, z_k (determined by the rate of the homogeneous reaction). For a very thin diffusion layers: $z_d < z_k$, halide anions leave the diffusion layer and react with XO_n^- anions only in the bulk solution. Both the polarization curve and the maximal current correspond to the electrode reaction of halogen molecules from the bulk solution, without a significant contribution due to the comproportionation reaction. In the intermediate range of the diffusion layer thickness: $z_k < z_d < 2n\ z_k$, the halide anions generated at the electrode are consumed mostly by this homogeneous reaction within a thin kinetic layer (located deeply inside the diffusion layer) while the halogen molecules produced by this reaction diffuse partially to the electrode, generating again halide anions. This combination of the chemical and electrochemical steps results in an autocatalytic cycle, based on the X^-/X_2 mediating redox couple, which consumes a significant amount of XO_n^- anions. The maximal current becomes much higher than the mass-transport of halogen from the bulk can sustain, depending essentially on the kinetic layer thickness. In the third range of the diffusion layer thickness: $2n\ z_k < z_d$, the amounts of the accumulated redox-couple components are so high that the principal (but non-electroactive) oxidant, XO_n^- is consumed within the external part of the kinetic layer with the maximal rate determined by the XO_n^- anion diffusion across the diffusion layer, which results in a very high maximal current proportional to the bulk concentration of XO_n^- anions. The theory predicts a complicated behavior of the maximal current as a function of the diffusion layer thickness (or the disk rotation rate for the RDE technique), with a maximum and a minimum separated by the range with an anomalous variation: increase of the maximal current with increase of the diffusion layer thickness (“autocatalytic interval”).

1. Introduction

One of the promising new directions in the area of high energy density and high power electrochemical energy sources for

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* Corresponding author.
E-mail addresses: mivo2010@yandex.com (M.A. Vorotyntsev), ruthenium2008@yahoo.com (Y.V. Tolmachev).

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stationary and transportation applications is based on *flow batteries* (see recent reviews [1,2]). Such devices possess important advantages compared to both fuel cells and to batteries with solid electroactive materials (SEAM). Flow batteries may not require precious metals for electrode materials, the desired energy and power can be scaled in an independent manner, they can be quickly mechanically recharged (refilled) etc. However, a large scale market adoption of flow batteries is hampered by certain drawbacks of the earlier proposed redox couples, the principal ones being a relatively low energy density, which makes them inferior to lithium-ion batteries in electric vehicles, and a low power density, which makes them too expensive for stationary energy storage.

Quite a novel approach in this area based on “high specific energy aqueous regenerative flow batteries” has been proposed recently [3–6]. The general underlying concept is to use a concentrated solution of an aqueous multielectron oxidant (AMO) in the cathodic compartment of the discharge cell. Such AMO is not subject to sufficiently rapid electrode reaction near its equilibrium potential, at least for inexpensive electrode materials. However, its reduction product is able to ensure simultaneously *two* functions: (1) to be a component of a *reversible redox couple*, (2) to participate in a sufficiently rapid *bulk-solution* comproportionation reaction with AMO, which results in generation of the second component of the reversible redox couple.

The discharge process may be illustrated by the example [4,6] where a concentrated aqueous solution of $LiBrO_3$ (13.27 *m* solubility at 20 °C) [7,8] is used as the oxidant and H_2 gas is used as the reducer. Although bromate (as well as chlorate) does not undergo a direct electroreduction in the potential range of interest on non-catalytic electrodes such as carbon, bromate electroreduction can be efficiently accomplished via its comproportionation with bromide, the product of this chemical reaction being bromine which may be transformed rapidly back into bromide at the cathode. The set of these coupled electrochemical and chemical steps inside the cathodic compartment is given by Eqs (1Br) and (2Br):

$$Br_2 + 2\ e^- \rightleftarrows 2\ Br^- \text{ on the cathode} \qquad (1Br)$$

$$BrO_3^- + 5\ Br^- + 6H^+ \rightarrow 3\ Br_2 + 3H_2O \text{ in the catholyte} \qquad (2Br)$$

The hydrogen electrooxidation taking place in the anodic compartment generates acidic protons that are transported across the membrane, for their consumption in reaction (2Br). Additional protons can be introduced (if needed) into the bromate-containing oxidant fluid by adding an acid from an external source or via the waste- and reagent–free Orthogonal Ion Migration Across Laminar Flow process akin to ion suppression of ion chromatography [4,6].

In addition to a high specific energy, the disclosed system is expected to be capable of providing a high areal power owing to the combination of fast homogeneous comproportionation (2Br) between the bromate reagent and the bromide product (owing to the sufficiently high solution acidity) and fast electrode reaction (1Br), thus resulting in the *mediated* electroreduction of bromate to proceed at the bromine reduction potentials with a high current density, thus overcoming the problem of a slow *direct* electroreduction of bromate on carbon [12–18]. Moreover, as shown below, very high current densities can be achieved at low (or even zero) bulk-solution concentrations of redox components, Br_2 and Br^-, since they are accumulated in the vicinity of the electrode via repetition of cycle (1Br-2Br).

This requirement to accumulate high concentrations of these redox components at the electrode surface imposes limitation on the intensity of the fluid motion. Its increase resulting in a thinner diffusion layer may lead to a rapid loss of the intermediate components (bromide and bromine) from the reaction layer, resulting in a decrease of the overall reaction rate. As shown below, this effect leads to drastic deviations from the conventional behavior in the Levich coordinates, the current might even *decrease* under a more active agitation of the solution. Since such anomalous features might also take place for other halogen derivatives, this paper presents a quantitative theoretical analysis of such processes for various halogen oxoanions, XO_n^- (n = 1, 2, 3 or 4), under steady-state conditions and a uniformly accessible electrode surface. Such situation may be realized e.g. at a rotating disk electrode.

2. Theoretical analysis

2.1. Various EC/EC’ mechanisms

The system under our study represents a particular case of a broad family of processes that are termed “EC mechanism” where the product of an electrochemical step (E) participates in a chemical reaction (C). In particular, steps E and C for bromate electroreduction are given by Eqs (1Br) and (2Br), respectively. Therefore, a brief overview of known systems belonging to this family [19] is provided below for the sake of their comparison with the processes under our study. To simplify their comparison with the novel results for our system the same notations are used here: C and B for the Ox and Red components of the redox couple, respectively, while species A can react with the product of the electrochemical step, B. Indices r and i means “reversible” or “irreversible” transformation, respectively. Notations of particular mechanisms below are given in conformity with book [19]

1 EC mechanism with reversible transformation, decay or irreversible catalysis described by reactions [19,20]:

$$E_rC_r\text{: } C + ne^- \rightleftarrows B,\ B \rightleftarrows P \text{ (non-reactive product(s))} \qquad (1EC)$$

$$E_rC_i\text{: } C + ne^- \rightleftarrows B,\ B \rightarrow P \text{ (non-reactive product(s))} \qquad (2EC)$$

$$(2\text{'EC}) \text{ or } C + ne^- \rightleftarrows B,\ B + A \rightarrow P \text{ (non-reactive product(s))}$$

2 EC mechanism with dimerization described by reactions [19]:

$$E_rC_{2i}\text{: } C + ne^- \rightleftarrows B,\ B + B \rightarrow D \text{ (non-reactive product)} \qquad (3EC)$$

3 EC mechanism with surface catalysis described by reactions for surface-confined species, C_{ads} and B_{ads} [19,21–23]:

$$C_{ads} + ne^- \rightleftarrows B_{ads},\ B_{ads} + A(0) \rightarrow C_{ads} + P(0) \text{ (non-reactive product(s))} \qquad (4EC)$$

4 EC mechanism with catalysis by solute redox mediator couple described by reactions [19,20,23–31]:

$$E_rC'_i\text{: } C + ne^- \rightleftarrows B,\ B + A \rightarrow C + P \text{ (non-reactive product(s))} \qquad (5EC)$$