

# Numerical studies of fundamental principles of ion transport in electrochemical systems based on autocatalytic redox–mediator mechanism

Antipov Anatoly Evgenievich

*D.Mendeleev University of Chemical Technology of Russia, Moscow, Russia*

A new autocatalytic EC'' mechanism of electrochemical reactions has been proposed recently [1]. Similar to the well-known electrochemical catalytic mechanism EC', the conversion of electrochemically inactive reagent is carried out due to its chemical reaction with one of the solute components of the mediating redox couple, but in the EC'' case the reagent is transformed into a component of this couple in the course of the reaction. As a result, accumulation of the homogeneous catalyst, i.e. of the mediating redox couple takes place, so that such a process has got autocatalytic features. A particular example of such EC'' mechanism is provided by the electroreduction of halogen oxoanions  $XO_3^-$  (for  $X = Cl, Br$  or  $I$ ), which in some cases passes by means of a combination of the electrochemical and chemical steps, namely a reversible transformation between the components of the redox couple:



while the oxoanion is reduced via comproportionation reaction:



For passage of a current,  $j$ , under steady state conditions the system of Eqs. (3) with boundary conditions (4) describes the concentration profiles inside the diffusion layer for such a reaction at the uniformly accessible electrode surface:

$$D_A d^2A/dz^2 = v, \quad D_B d^2B/dz^2 = 5v, \quad D_C d^2C/dz^2 = -3v, \quad v = k A(z) B(z) \quad \text{for } 0 < z < z_d \quad (3)$$

$$A(z) = A^0, \quad B(z) = 0, \quad C(z) = C^0 \quad \text{for } z = z_d; \quad dA/dz = 0, \quad D_B dB/dz = -j/F, \quad D_C dC/dz = j/2F \quad \text{for } z = 0 \quad (4)$$

Eqs. (3) may be partially integrated, resulting in analytical relations between each pair of concentrations. Then, this system of equations and boundary conditions may be reduced to the equations for dimensionless concentrations:

$$d^2b(x)/dx^2 = a(x)b(x), \quad a(x) = 1 - J[x_{dk} - x - b(x)]/x_{dk}, \quad c(x) = 0.1[x_{dk} - x - 6b(x)] \quad \text{for } 0 < x < x_{dk} \quad (5)$$

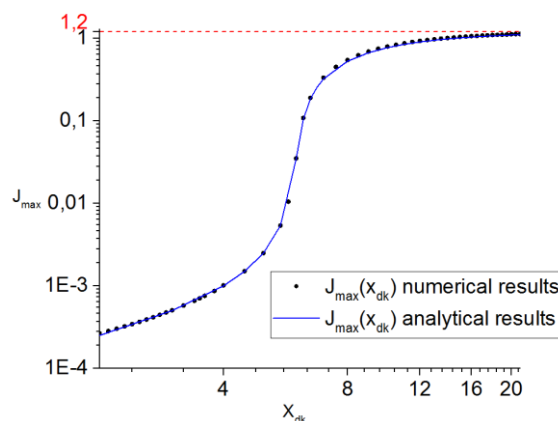
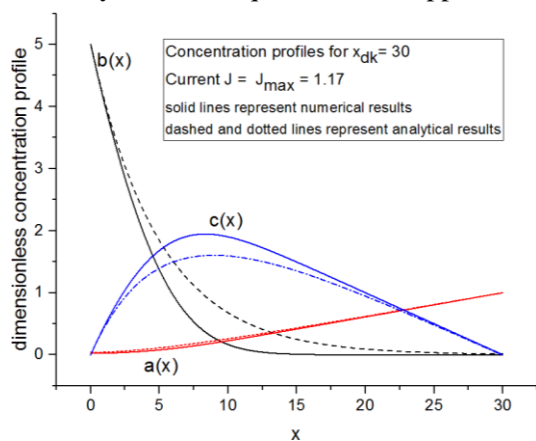
where  $x \equiv z/z_k$ ,  $x_{dk} \equiv z_d/z_k$ ,  $z_k \equiv (D_A/5kA^0)^{1/2}$ , kinetic layer thickness,  $J$ , dimensionless current density.

Eqs. (5) are combined with conditions at two boundaries:  $b(x_{dk}) = 0$ ,  $db/dx = -1$  for  $x = 0$ .

Its solution was found by choosing a trial value:  $b(0) = b_0$ , to perform the numerical integration of Eqs. (5) with the use of the Runge-Kutta routine. Thus found  $b(x_{dk})$  value served to determine the next  $b_0$  value, in order to approach  $b(x_{dk})$  stepwise to 0. This test and trial procedure provided the concentration profiles for any combination of the  $x_{dk}$  and  $J$  values. The solutions must also satisfy to the condition that no concentration is negative within the whole  $x$  interval. The maximal current density,  $J^{max}$ , was found for each  $x_{dk}$  value from the condition that one of the concentrations becomes equal to 0 in a point (Fig. 1).

These numerical results were compared with approximate analytical formulas, which had been derived in [1]. Excellent agreement was found for relatively weak current densities. Numerical and analytic results for the  $J^{max}(x_{dk})$  dependence are very close to each other even for the range of very strong currents (Fig. 1). On the other hand, marked difference has been discovered in the latter case for the concentration profiles (Fig. 2).

Thus, one may conclude that the numerical approach carried out in this study represents a very prospective method both for verification of approximate analytical results (where they may be obtained) and for theoretical predictions for regimes where analytical technique cannot be applied.



**Fig. 1 (on the right)** The maximal current density,  $J^{max}$ , as function of  $x_{dk}$ .

**Fig. 2 (on the left)** Profiles of dimensionless concentrations for of  $XO_3^-$ ,  $X^-$  and  $X_2$  species (denoted as  $a(x)$ ,  $b(x)$ ,  $c(x)$ , correspondingly).

## References:

1. M.A.Vorotyntsev, D.V.Konev, Yu.V.Tolmachev, *Electrochim. Acta*, 2015, DOI.org/10.1016/j.electacta.2015.06.076