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Visual modelling electrochemical processes

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ABSTRACT

Visual modelling assumes a graphic form of model description and visual representation of research results. The main element of modelling system representation is a block diagram. Owing to appearance of this line of investigation («object-oriented modelling») a software was produced (for example, Simulink in MatLab).

The examples of ordinary differential equations solving schemes for initial stage discharge of lead-acid battery positive electrode visual modelling are presented. The comparative analysis of two algorithms (a shooting method and algorithm similar to back propagation algorithm used in the neural networks theory) also is carried out.

1. Introduction

During theoretical description of battery discharge process, there are difficulties connected with the fact that owing to the porous structure the process proceeds on all electrode plate thickness, and the discharge characteristics casually vary from point to point. It is also necessary to take into account that in the lead-acid battery a non-uniform accumulation of poorly soluble and poorly conducting reaction product occurs at the plate thickness, that results in non-uniform distribution of the discharge characteristics (electrolyte concentration, overvoltage, distribution of reaction product etc.) at the electrode thickness. As a rule boundary value problem numerical solving is necessary.

Last decades some new directions of problem investigation, including electrochemical problems, have been appeared:

- visual modelling;
- artificial intelligence methods, including an artificial neural networks (ANN) formalism and genetic algorithms [1,2]. Analogue of such biologically motivated approaches is also new direction, which has arisen in 90 years – artificial immune systems (AIS) formalism. In particular, the AIS method allows with good accuracy to find local and global maxima of multimodal functions, that it is practically impossible to make with using traditional methods [3];
- application of calculus mathematics modern systems, including symbolical algebra systems.

The visual modelling assumes using graphic form of model description and evident representation of research results. In connection with this direction of investigation the term "object-oriented modelling" (OOM) appeared and the appropriate software in modern calculus mathematics systems was created. Now the most popular visual modelling system is Simulink (MatLab package). A package VisSim also received the wide distribution. It would be desirable to note the developments of the Russian programmers (St.-Petersburg Polytechnical University): AnyLogic [4] and Model Vision Studium (MVS) [5].

In OOM a basic element of simulated system graphic representation is the block diagram. The mathematical diagram and, if necessary, 2D and 3D animation is used for result representation.

Advantage of the given approach is using the object-oriented approach including presentation and modules of the appropriate algorithms, solving schemes construction and also easier understanding of computing schemes by the researchers who are not having programmer skills.

The graphic means of the appropriate software allow to observe visually the process of system characteristics calculation and bring in the appropriate corrections into the model. In electrochemical problems the researched characteristics could be, for example, electrolyte concentration or electrochemical reaction rate distributions on the electrode thickness.

In the article the examples of electrochemical processes visual modelling are considered including modelling in MATLAB Simulink.

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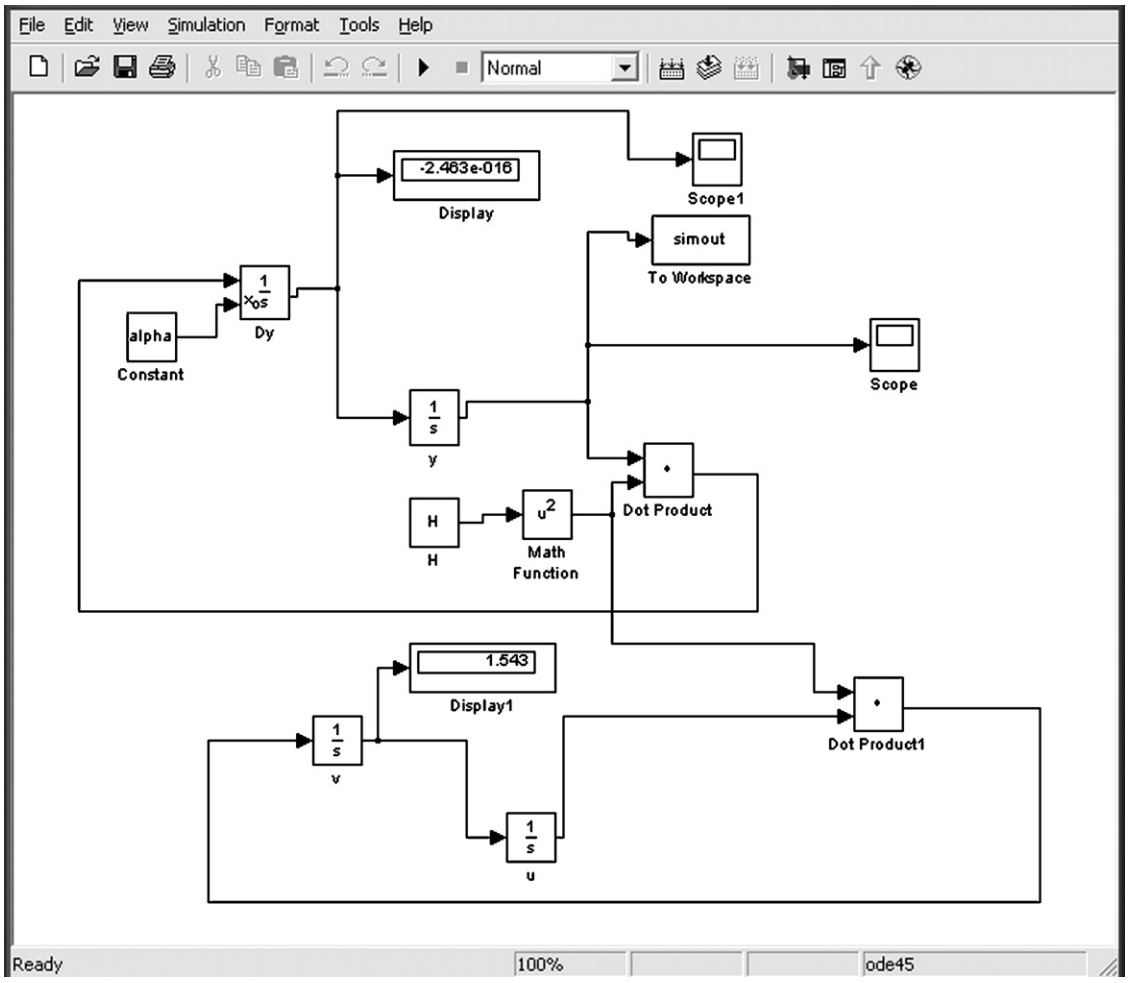

Fig. 1. The scheme of a Koshi problem (4) and (6) solution in Simulink.

2. Boundary problem solution in Simulink

Let's consider a technique of drawing up differential scheme in Simulink for the Koshi problem decision arising from the description of such processes as "reaction–diffusion" ones. In dimensionless form it is possible to present governing differential equation in a form

$$d^2y/dx^2 + (p/y)\,dy/dx = H^2y, \tag{1}$$

where H is dimensionless parameter and p is a parameter reflecting problem geometry ($p = 0$, 1, 2 for rectangular, cylindrical, spherical coordinates, respectively).

At $p = 0$ Eq. (1) has a form

$$d^2y/dx^2 = H^2y, \tag{2}$$

where y is a dimensionless concentration of liquid reagent.

In particular, Eq. (2) describes quasi steady-state process such as "reaction–diffusion" in porous media. Dimensionless parameter H can be presented as $H = (L/\xi)$, where ξ is the reaction zone effective depth (i.e. distance from a surface in a plate where the reaction rate is appreciably distinctive from zero). Parameter H depends on properties of a plate material, properties of reagent solution and chemical reaction rate inside a plate. The concept of effective reaction zone depth was introduced by Ya. B. Zeldovich for the theoretical description of catalyze process in a porous plate.

Let's solve problem (2) with the boundary conditions:

$$y(0) = 1, \quad \frac{dy}{dx}(1) = 0. \tag{3}$$

It is supposed that $x = 0$ corresponds to a surface and $x = 1$—to a centre of a plate.

Let's solve a problem (2) with boundary conditions (3) by the shooting method.

Let's put to a problem (2)–(3) in conformity with a Koshi problem:

$$\begin{aligned} &dy/dx = f, \\ &df/dx = H^2y, \\ &y(0) = 1, \quad f(0) = \alpha. \end{aligned} \tag{4}$$

where α is an unknown parameter.

To find a parameter α it is necessary to solve the non-linear equation

$$\left.\frac{dy}{dx}(x, \alpha)\right|_{x=1} = 0. \tag{5}$$

Here $y(x,\alpha)$ is the values of y received as a result of the numerical decision of system (4) at fixed value of α.

Let's enter notation: $\partial y/\partial\alpha = u$, $\partial f/\partial\alpha = v$. Differentiating ordinary differential equation (ODE) system on parameter α, we shall receive

the ODE system:

$$du/dx = v,$$
$$dv/dx = H^2 u, \quad (6)$$
$$u(0) = 0, \quad v(0) = 1.$$

The scheme of the Koshi problem decision (4) and (6) in Simulink is shown in Fig. 1.

To search a suitable value of parameter α we create a M-file in MATLAB with the text of the program:

```
H=10; alpha=0.5; fend=0; alphaOld=1; eps=1.*10^(-6);

sim('Plate')

while (abs(alphaOld-alpha)>=eps)

alphaOld=alpha;

sim('Plate')

fendCalc=xFinal(1); vend=xFinal(2);

alpha=alpha-(fendCalc-fend)/vend;

end

sim('Plate')
```

Here Plate is a file name with the scheme in Simulink.

For $H = 10$ after the program work termination we receive the graph of $y(x)$ shown in Fig. 2.

Changing values of H we receive the appropriate decisions (Fig. 3) which are well agreed with the given ones in refs. [6,7] and also with the analytical decision $y = \cosh[H(1-x)]/\cosh(H)$.

From Fig. 3 it is well seen that at small H the reagent concentration distribution becomes practically homogeneous on all thickness of a plate, and at increase H the reaction is replaced in the superficial layers of a plate. In lead-acid batteries the similar reagent behavior during the dicharge results in strongly non-uniform distribution of a reaction product on electrode thickness at a final discharge stage.

3. Visual modelling lead-acid battery discharge initial stage

As an example we consider the numerical schemes of current density and overvoltage initial distribution modelling in Simulink of a package MATLAB.

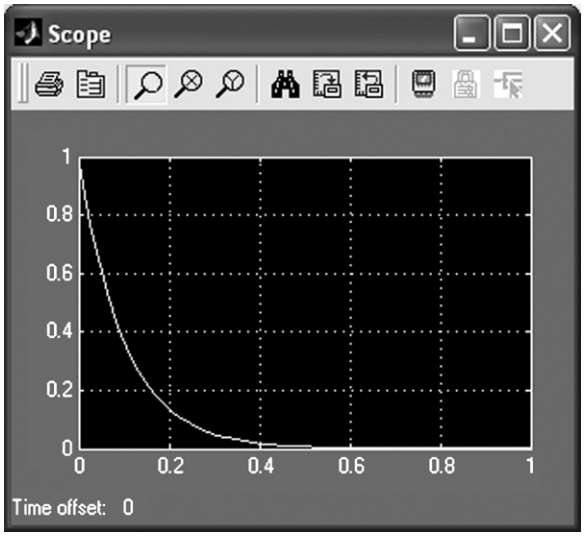

Fig. 2. The graph of a Koshi problem (4) and (6) solution.

The soluble system ODEs has a form:

$$d\eta/dz = i/A, \quad (7)$$

$$di/dz = g(1 - 2\eta). \quad (8)$$

with boundary conditions

$$\eta(0) = 0, \quad (9)$$

$$i(0) = 0, \quad (10)$$

$$i(1) = 1, \quad (11)$$

where dimensionless parameters and variables are

$$z = x/L, \quad i = i_2/I, \quad \eta = \eta' F/RT, \quad A = k_0 RT/ILF.$$

There L is a half of electrode plate thickness, m; I is an overall discharge current density, A m^{-2}; i_2 is a current density in a porous electrode, A m^{-2}; η' is overvoltage, V; R is an universal gas constant, J mol^{-1} K; T is temperature, K; F is Faraday constant, A s kg-eq.; k_0 is the electrolyte conductivity under initial conditions, Ω^{-1} m^{-1}.

The system (7)–(11) is a special case of more general ODE system for the lead-acid battery positive electrode discharge process description [8]. It is supposed, that in the discharge beginning electrolyte concentration, porosity and electrolyte conductivity are constant, and the discharge product is absent.

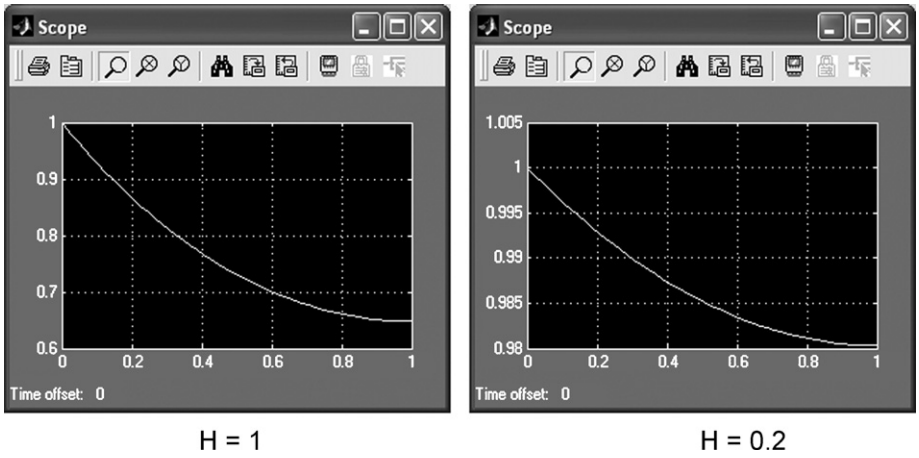

Fig. 3. The distribution of the reagent concentration inside the plates of various thicknesses.

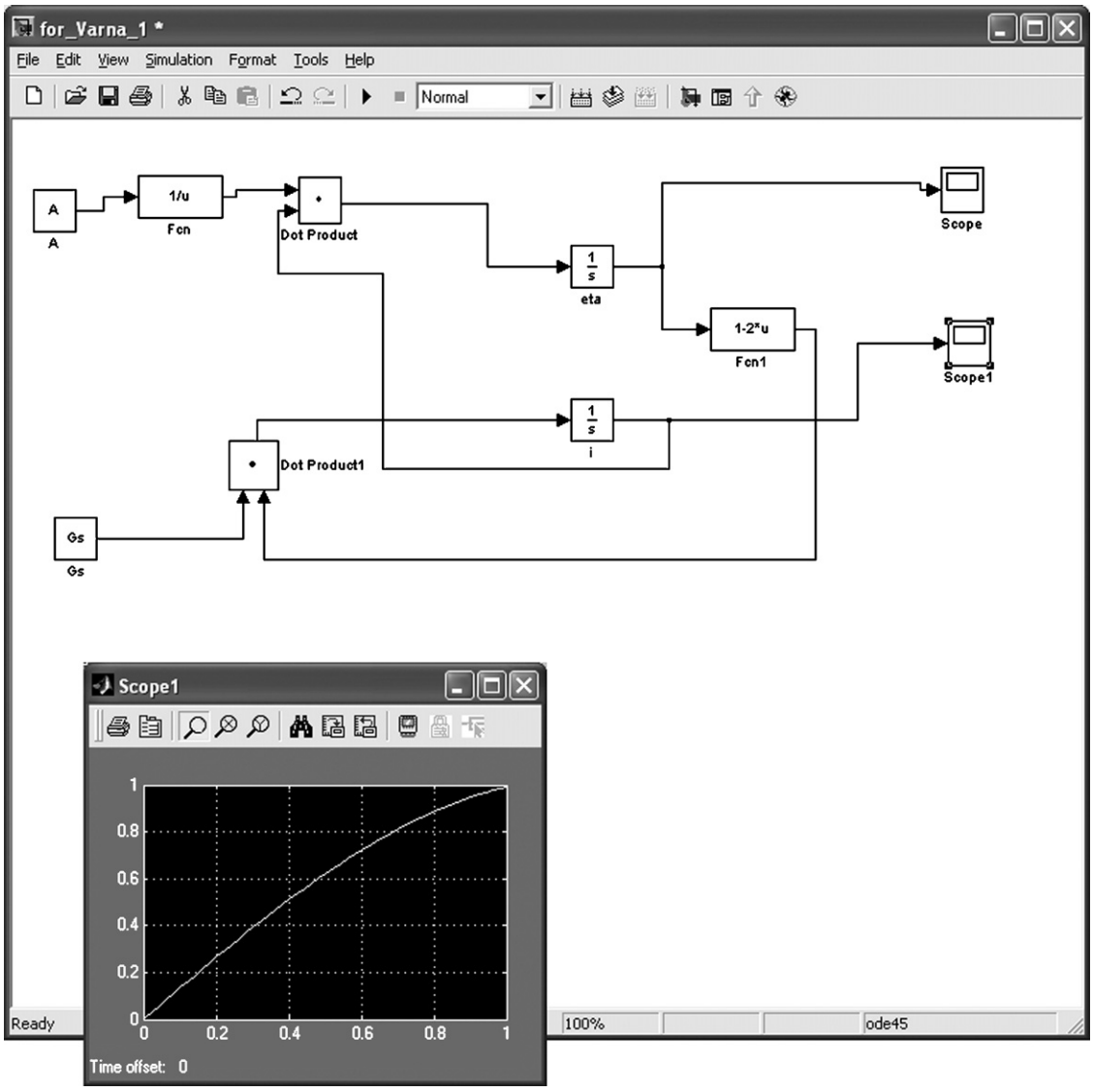

Fig. 4. The scheme of ODE system solution for an initial stage of the lead-acid battery discharge.

The presence of three boundary conditions is caused by the fact that the system of two linear equations (1) and (2) contains unknown parameter g, which reflects a current exchange density dependence on phenomenological parameters (initial specific surface area of electrode active material, exchange current density etc.), therefore one boundary condition is used for numerical value definition of parameter g.

The scheme of the ODE system decision (1)–(2) as Koshi problem with the initial conditions (3)–(4) is shown in Fig. 4.

With the help of given scheme it is possible to quickly "play" various variants to find "manually" value of parameter g close to correct one. Having added two equations in scheme it is possible to automate parameter selection process. For this purpose we add two differential equations for variable $u = \partial\eta/\partial g$ and $v = \partial i/\partial g$ in system under consideration by differentiation the equations (12)–(13) on the parameter g with the initial conditions $u(0) = 0$ and $v(0) = 1$. After the decision of the Koshi problem we receive the values of $i(1)$ and $v(1)$. In a shooting method the value of parameter g is corrected under the iterative formula of Newton–Rafson:

$$g_{\text{new}} = g_{\text{old}} - [i(1) - 1]/v(1), \tag{17}$$

where g_{new} and g_{old} are the values of parameter g on the current and previous iteration accordingly.

In the simple case the visual modelling schemes could be created using spreadsheets Excel with the built-in programming language Visual Basic for Applications (VBA).

As an example the scheme to calculate initial distribution of current density and overvoltage in neural network basis on a 1st order Runge–Kutta method in the spreadsheets Excel is partially shown in Fig. 5.

The neural network basis represents the weighed summation of several entrance signals operation with the subsequent transformation of this sum by means of formal neuron activation function which can be both linear and non-linear.

In particular, for system of two equations and the 1st order Runge–Kutta method we receive the formulas:

$$y_{1,t+1} = b_{11}y_{1,t} + b_{12}y_{2,t} = (1 + ha_{11})y_{1,t} + ha_{12}y_{2,t},$$
$$y_{2,t+1} = b_{21}y_{1,t} + b_{22}y_{2,t} = ha_{21}y_{1,t} + (1 + ha_{22})y_{2,t}.$$

Here $y_{i,t}$, $y_{i,t+1}$ is the decision of ODE system at step t and $t+1$ accordingly. Similar expression could be turned out for a Runge–Kutta method of higher orders.

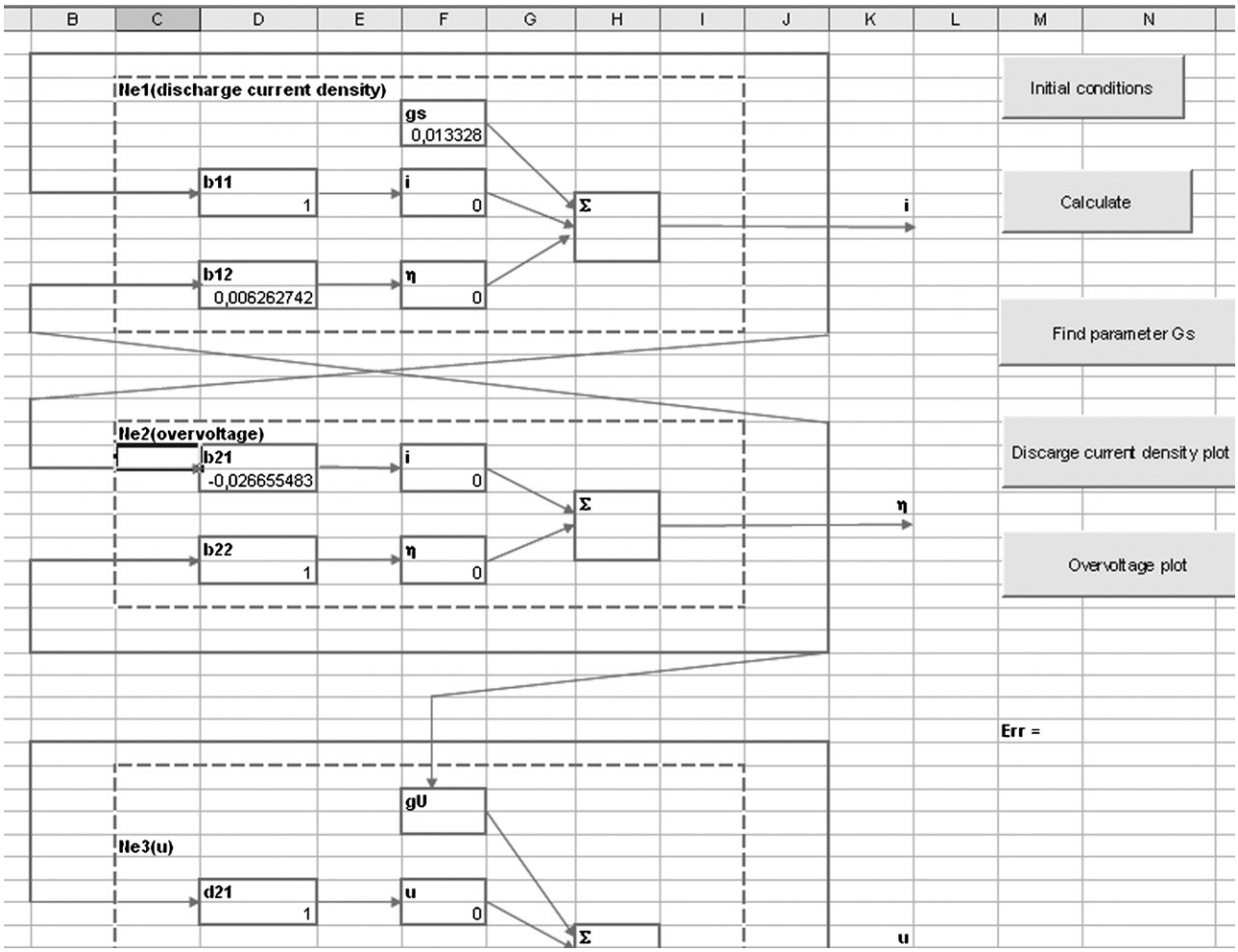

Fig. 5. The scheme of ODE system solution in a neural network basis.

We see that the expression in the right part represents the weighed sum with a weight matrix

$$\omega = \begin{pmatrix} 1 + ha_{11} & ha_{12} \\ ha_{21} & 1 + ha_{22} \end{pmatrix}.$$

The scheme is shown after installation of problem initial values. The scheme enables to lead search of parameter on one of two algorithms: shooting algorithm and offered by us algorithm similar to the back propagation algorithm in ANN formalism. Then minimized functional will have a form $(1/2)\cdot[i(1)-1]^2$ and we will receive a recurrence formula

$$g_{\text{new}} = g_{\text{old}} - \gamma[i(1)-1]v(1), \tag{18}$$

where γ is a parameter of training.

The iterations come to an end when the difference of parameter g values on the current and previous steps becomes less than the given value.

The comparison of the formulas (17) and (18) shows that it is to be expected the best convergence of back propagation algorithm especially when the value of $v(1)$ is small enough. The calculations show that the algorithm convergence rate is sensitive to the value of parameter γ and in the calculus error of value of $i(1)$ is less by the order of magnitude in comparison with the shooting method.

From Fig. 5 the opportunity of parallel calculations is well seen during the numerical decision of the given problem when the separate program parts could be carried out independently on different computing devices.

There is also other approach to the decision of ODE problems based on a neurocomputing [9].

4. Conclusions

Some new methods of the differential equations systems solving are briefly considered. Similar problems are often occur at modelling various processes including electrochemical ones.

The algorithm of solution is offered which is similar to the back propagation algorithm used for training artificial neural networks. The comparison of this algorithm with shooting one was made for the problem of lead-acid battery positive electrode discharge modelling. It is shown that the rate of algorithm convergence depends efficiently on the value of parameter of training and at a suitable choice of given parameter the algorithm works faster and the calculation error is less by the order in comparison with shooting algorithm.

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