Research on Activated Carbon Supercapacitors
Electrochemical Properties Based on Improved PSO-BP Neural Network

Xiaoyi Liang¹, Zhen Yang¹,², Xingsheng Gu³ and Licheng Ling¹

Abstract: Supercapacitors, also called electrical double-layer capacitors (EDLCs), occupy a region between batteries and dielectric capacitors on the Ragone plot describing the relation between energy and power. BET specific surface area and specific capacitance are two important electrochemical property parameters for activated carbon EDLCs, which are usually tested by experimental method. However, it is misspent time to repeat lots of experiments for EDLCs’ studies. In this investigation, we developed one theoretical model based on improved particle swarm optimization algorithm back propagation (PSO-BP) neural network (NN) to simulate and optimize BET specific surface area and specific capacitance. Comparative studies between the predicted data and experimental data—earlier deduced by Liu et al, have revealed that improved PSO-BPNN model bears higher prediction accuracy, faster computation speed and better generalization performance. It is concluded that the improved PSO–BP NN is one simple and effective method to find optimal conditions of BET specific surface area and specific capacitance for activated carbon EDLCs.

Keywords: Activated Carbon EDLC; Electrochemical Property; Neural Network; Particle Swarm Optimization

1 Introduction

In recent years, it has aroused lots of interest in supercapacitors (EDLCs) because they fill in a gap between batteries and conventional capacitors in terms of energy and power EDLCs have been touted as a solution to the mismatch between the fast
growth in power required by devices and the inability of batteries to efficiently dis-
charge at high rates [Chmiola, Yushin, Gogotsi, Portet, Simon and Taberna (2006);
Arico, Bruce, Scrosati, Tarascon and Schalkwijk (2005)]. This large capacity for
high power discharge is directly related to the absence of charge-transfer resis-
tances that are characteristic of battery faradaic reactions and subsequently leads to
better performance at low temperature. Improvements in the energy density may
accelerate the advent of electrical and fuel-cell cars, as well as enable numerous indus-
trial and consumer applications for supercapacitors [Brodd, Bullock and Leising
(2004)]. The main classes of the EDLCs are activated carbon, nano-carbon fiber
and carbon aerogel, etc. Among of them, activated carbon has been applied widely
because it have many advantages of cheap cost, easy to access and consistent per-
formance.

BET specific surface area and specific capacitance are two important parameters
that affect the electrochemical performances (mainly including energy density and
power density) of activated carbon EDLCs. During the process of searching for
relationship between the technical parameters and desired performance indicators
of EDLCs lots of experiments have to be repeated. Such traditional material design
method would be bound to waste lots of manpower and resources. However, theo-
retical modeling offers reasonable alternative because total or part of complex and
time-consuming experiments can be replaced[Yang, Gu and Liang (2007); Husain,
Guniganti, Sehgal and Pandey (2009)].

Recently, with the development of modern science and technology, artificial intel-
ligent technology has been widely used to predict, estimate and optimize for ma-
terial engineering[Aymerich and Serra(2006); Kerh, Lai, Gunaratnam and Saun-
ders(2008); Wu, Chiu and Wang (2008)]. BPNN(Back Propagation Neural Net-
work) and PSO (Particle Swarm Optimization) algorithm are two branches of arti-
ficial intelligence technology that can be combined to optimize complex non-linear
problems [Pidaparti and Neblett(2007)]. In this paper, we proposed a new improved
PSO algorithm to optimize electrochemical properties of activated carbon EDLCs.
It is found that the improved PSO–BPNN has great potential to handle problems
such as estimating and optimizing variables in material chemometrics systems.

2 Experimental process

2.1 Activated Carbon Preparation

A series of activated carbon EDLCs samples, including $A_1 \sim A_{18}$ and $B_1-B_5$ were
prepared by means of KOH activation method. The pitch coke powder and KOH
solution were mixed with different ratios of alkali / carbon in different heat treat-
ment processes at different activation times. The mixture should be mixed fully,
and then was activated from 700°C to 830°C under nitrogen protection in a nickel autoclave.

2.2 Activated Carbon Electrodes Preparation and Simulation Capacitor Assembly

60% Polytetrafluoroethylene (PTFE) emulsion was added to the electrodes materials as binder and the mass ratio of activated carbon and PTFE was fixed at 95:5. In an agate grinder, the mixture was milled for two hours in order to obtain a homogeneous product. Then, the mixture was kneaded and pressed to shape the round slices electrodes with 13.3mm long and 0.5mm thick by hydraulic machines at 10MPa. The carbon electrode films were made by suppressed carbon film on the nickel foam (100ppi) collector. In an argon glove box, the two equal mass of nickel electrode films were laid face to face and interrupted by polypropylene (PP) septum. Before assembling into simulation capacitors, carbon electrode and PP septum were immersed in a vacuum electrolyte. Finally, they were assembled into a simulated capacitor. The process chart of EDLC electrode was shown in Figure 1.

![Figure 1: The process chart of EDLC electrode](image)

2.3 Methods of BET Specific Surface area and Specific Capacitance Test

Specific surface area of EDLC electrode was tested by multipoint BET method and the BET specific surface area was measured by Micromeritics ASAP2020. Constant current charge-discharge circulating was tested with DTS which is a kind of high-precision capacitors test system. The range of charge voltage was 0.05V ~0.9 V and the number of charge and discharge circulating was more than one hundred. We obtained the specific capacitance of activated carbon simulation capacitor
according to [Qu and Shi (1998)]:

\[ C = 2I(m \times \Delta V/\Delta t), \]  

(1)

where \( I(A) \) is the discharge current, \( m(g) \) is the mass of single carbon electrode and \( \Delta V/\Delta t \) is the slope of constant current discharge.

### 2.4 Experiment Data

BET specific surface area or \( S_{BET} \) and specific capacitance of activated carbon EDLCs were determined by lots of factors. In this study, we focused on three key factors: activation dosage, activation time and activation temperature. The practice for producing activated carbon EDLCs showed that selecting appropriate activation dosage, activation time and activation temperature can effectively adjusting and controlling experiment condition, achieve good technical parameters. Technical parameters of experimental samples were listed in Table 1.

### 3 BP Artificial Neural Networks

Artificial neural network or NN was founded by McCulloch and Coworkers in early 1940s [Perlovsky (2001)]. NNs had emerged as a result of simulation of biological nervous system (such as the brain) on a computer. Nowadays, as one of the most powerful computer analysis techniques, neural networks have been used in many fields. By way of researching the application of nerve network technique, lots of the computer neural network models were established [Gorynin and Ushkov (2000)].

Materials chemometrics involves the relationships among components, process, organization and performance. However, it is difficult to establish mathematical model due to complex and unclear internal laws of material system. To overcome this problem, NNs use samples data to establish material intelligent system models. NNs have many advantages such as strong ability of nonlinear approximation, self-learning and so on. More importantly, NNs have the ability to solve multi-parameter and multi-step prediction problems. Just for that, NNs are very suitable for materials chemometrics problems.

There are dozens of neural network model such as BP, Radial Basis Function or RBF, Kohonen, Hopfield and Generalized Regression Neural Network or GRNN. Among of them, BPNN is the most extensive and practical one. The vast majority of neural networks are rooted in the standardized BP algorithm. Figure 2 showed the typical structure of BPNN[Yuan (2002)]. BP neural network is usually comprised by three layers. The first layer is input layer consisting of a group of processing units which are responsible for acceptance of data imported to the net-
work. The output layer is responsible for output data to the network. Other layers which do not accept any input data or output data are called hidden layers.

In Figure 2, supposing that $w_{ji}^l$ is connection weight from i node of $l−1$ layer to j node of $l$ layer, $net_{ji}^l$ and $out_{ji}^l$ are input and output values of j node of $l$ layer, $X_i (i=1,\cdots,N)$ is input factor, $f$ is neurons activation function. Usually, BPNN is
Output target
Output layer (NO.L)
Hidden layer
(NO.2~ NO.L-1)
Input layer (NO.1)
Input factor

Figure 2: Basic structure of BPNN

represented by following model:

\[
out_j^1 = x_j \quad (j = 0, 1, \ldots, N) \quad (2)
\]

\[
net_j^l = \sum_{i=0}^{pot(l-1)} \omega_{ji}^l out_i^{l-1} \quad (l = 2, 3, \ldots, L) \quad (3)
\]

\[
out_j^l = f(net_j^l) \quad (j = 1, 2, \ldots, pot(l)) \quad (4)
\]

\[
\hat{E}_j = out_j^L \quad (j = 1, 2, \ldots, M) \quad (5)
\]

Here, \(pot(l)\) \((l = 1, 2, \cdots, L)\) in Eq.(4) is the node number of each layer \(\hat{E}_j\) is estimated value of design objective. In BPNN, hidden layers error is determined by back propagating algorithm. BP algorithm is repeated several times until obtaining reasonable residual error. Steps of optimization procedure are similar to those detailed in [Guessasma, Montavon, Gougeon and Coddet (2003)] and the learning algorithm is detailed in [Hamzaoui, Guessasma, ElKedim and Gaffet (2005)].

4 Improved Particle Swarm Optimization Algorithm

The particle swarm optimization algorithm was first put forward by Kennedy and Eberhart[Eberhart and Kennedy (1995)] who was inspired by the swarming behavior of animals and human social behavior. In PSO algorithm, a point in the problem space is called a particle which consists of a position vector \(\vec{x}\) and a velocity vector \(\vec{v}\). Each particle’s position property is treated as a solution in D-dimensional space. Each particle is ‘flown’ through the multidimensional search space and adjusts its position according to its own experience and those of neighboring particles. The performance of each particle is evaluated by a predefined fitness function.
PSO is initialized by a group of random particles with different positions property and velocities property. The optimal solution is obtained through iteration. The two ‘extremes’ are the best position $\vec{p}$ obtained by the particle so far and the overall best position $\vec{p}_g$ obtained by all particles. Two ‘extremes’ are updated in each iteration. The updates of each particle consist of velocity update and position update. Usually, the particle position is updated according to:

$$\vec{x}(t + 1) \leftarrow \vec{x}(t) + \vec{v}(t + 1),$$

(6) and the velocity is updated according to:

$$\vec{v}(t + 1) = \omega \vec{v}(t) + \varphi_1 (\vec{p} - \vec{x}(t)) + \varphi_2 (\vec{p}_g - \vec{x}(t)),$$

(7)

where $\varphi_1$ and $\varphi_2$ are accelerated coefficient used to adjust the $\vec{v}_g$ and $\vec{v}$ respectively. They are often selected as random numbers typically within $[0,2]$. $\omega$ is the nonlinear variation inertia weight that represents speed inertial of particles.

In this work, step expression is replaced by Eq.(8):

$$\vec{x}(t + 1) \leftarrow c_1 \text{rand}_1 \vec{x}(t) + c_2 \text{rand}_2 \vec{v}(t + 1),$$

(8)

where $c_1$ and $c_2$ are step coefficients which are used to adjust the $\vec{x}_g$ and $\vec{x}$ respectively. To accelerate convergence rates and improve numerical precision, $c_1$ and $c_2$ often are selected as 2. $\text{rand}_1$ and $\text{rand}_2$ are random numbers typically within the limits of $[-1,1]$. In comparing improved variable step length PSO algorithm with the traditional PSO, improved PSO has following advantages: straight-forward logic, easy implement, few parameters to adjust and rapidly convergence rates because the step length is controlled by the autocorrelation estimation of error signal. Improved variable step length PSO algorithm constantly updates using Eq.(7) and Eq.(8) until specified number of iteration is exceeded or the particle velocity is close to zero.

5 Improved Particle Swarm Optimization Neural Network Model

Gradient algorithm has been widely used for training the weights of feed forward neural networks. BP algorithm has strong ability of searching for local optimal, however it is difficult for BP algorithm to get the global optimization as BP is a kind of gradient-based method. The weight is often updated according to:

$$\omega_{ji}^N(k) = \omega_{ji}^N(k - 1) + \Delta \omega_{ji},$$

(9)

where $N$ is the number of input node and $K$ is the number of iteration. As usual, BP algorithm has exposed these shortcomings: slowly convergence training speed,
6 PSO-BPNN Predicting Model for Activated Carbon EDLC’s Electrochemical Properties

The main process and method of PSO-BPNN predicting model for activated carbon EDLC electrochemical properties were as follows.

6.1 BPNN Predicting Model

In order to predict activated carbon EDLC electrochemical properties, a mathematical model expressed electrochemical properties in terms of experimental data was required. In this study, the mathematical model was built using BP neural network. During the BPNN model design process, we focused on the following aspects:

a. Experimental Database. The first step of BPNN modeling was to build an input-output training database according to activated carbon EDLC electrode experimental data. The experiment process was detailed in section 2 of this paper. The experimental database was used to train and test BPNN model.

b. Input-output Vector. In order to identify input vector, influence factors about activated carbon EDLC electrochemical properties should be carefully analyzed. There are lots of influential factors and their mutual influences are even strong. How-
ever, among of them, activation dosage, activation time and activation temperature are three key factors, so they were all selected as input vectors. Output vectors are BET specific surface area ($S_{BET}$) and specific capacitance.

The first 18 experimental data (No.A1 to No.A18 in Table 1) were used to train BPNN model, while the last 5 data (No.B1 to No.B5 in Table 1) were used to test BPNN model. In order to eliminate dimension different, all input and output data were normalized with the Eq.(10):

$$X_{norm} = \frac{2(X - X_{\text{min}})}{X_{\text{max}} - X_{\text{min}}} - 1. \quad (10)$$

All input and output data are mapped to the range of [-1,1].

c. Transfer Function Selection. How to select transfer function and activation function of BPNN is important. There are many transfer functions for neural networks such as logarithmic, tangent hyperbolic and gauss. In this paper, among these transfer functions, tangent hyperbolic sigmoid (tansig) led to the minimum mean square error (MSE) and was selected as hidden layer transfer function therefore. Because log-sigmoid(logsig) function mapped neurons value well to [0,1], and it was selected as output layer transfer function. Tansig function was represented as follow:

$$f(x) = \frac{2}{1 + e^{-2x}} - 1. \quad (11)$$

Logsig function was represented as follow:

$$f(x) = \frac{2}{1 + e^{-2x}}. \quad (12)$$

d. Number of Hidden Layer Neurons. NN training seems to be highly sensitive to number of hidden layer neurons; however, the number of hidden layer neurons is usually determined by trial and error. It is known that too few neurons can lead to under-fitting whereas too many neurons can contribute to over-fitting. In this work, gradually growth method was used to train network until the number of hidden layer nodes met the requirements of error. During training process, number of hidden layer neurons had been increased from 5 to 9 in order to define output accurately. Statistical methods were used to compare the training results. Mean-squares error (MSE) was defined as follows:

$$MSE = \frac{1}{mp} \sum_{p=1}^{m} \sum_{s=1}^{p} (d_{ps} - y_{ps})^2, \quad (13)$$

where m is the number of output nodes, p is the number of training sample, $d_{ps}$ is desired output value of NN model and $y_{ps}$ is actual output value of NN model.
Figure 3 illustrated the performance of BPNN training with different numbers of hidden layer neurons. As seen from Figure 3, when the number of hidden layer neurons was 6, it met the requirements of model design because MSE of the NN model was close to 0.0012 and gradually fell to 0.001 after 150 epoch. Hence 6 were set as optimal number of hidden layer neurons.

![Figure 3: Relationship diagram among MSE, number of hidden layer neurons and iteration epochs](image)

6.2 Optimized PSO-BPNN Predicting Modeling

BPNN structure was composed of three layers: three input layer neurons corresponding to activation dosage, activation time and activation temperature, two output layer neurons corresponding to BET specific surface area and specific capacitance and one hidden layer with 5-9 neurons. Table 2 summarized learning factors of BPNN model during training and testing processes.

<table>
<thead>
<tr>
<th>Parameter item</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Learning rate ($\eta$)</td>
<td>0.04</td>
</tr>
<tr>
<td>Momentum constant</td>
<td>0.9</td>
</tr>
<tr>
<td>Maximum number of epochs</td>
<td>500</td>
</tr>
<tr>
<td>Goal of MSE</td>
<td>0.01</td>
</tr>
</tbody>
</table>
In PSO-BPNN model, all particles were encoded by real number strings. Each real number string represented weights of BPNN model. The improved PSO–BP predicting and optimizing modeling approach of activated carbon EDLCs’ electrochemical properties can be described as follows:

Step 1. Set parameters for improved PSO.
This step included setting the numbers of PSO particles, dimension D, randomly initial string with adaptive group-scale, the initial $w$, learning factor $c_1$, $c_2$ and iteration stop conditions. In this study, $s$ was set as 18, $D$ was set as 47, $w$ was set as 0.6, $c_1$ and $c_2$ were set as 2 and largest iterative number was set as 500.

Step 2. Calculate the fitness function value according to Eq.(14)

$$J = \frac{1}{2} \sum_{n} \sum_{k} (Y_n,k - \bar{Y}_{n,k})$$

(14)

If the function value met certain conditions, training process would be terminated and we obtained output results. Otherwise the fitness information will be returned to the next step.

Step 3. Update $\omega$ according to fitness function.

Step 4. Return to the second step and calculate the new fitness with renewed $\omega$.

Step 5. Get optimal solution.
When iteration was terminated, an improved PSO-BP algorithm was obtained based on initial optimal solution of improved PSO algorithm.

Step 6. The optimized PSO-BPNN model was used to predict activated carbon EDLCs’ electrochemical properties.

6.3 PSO-BPNN Testing
The performance of trained PSO-BPNN model can be evaluated by errors of train and test sets. The PSO-BPNN model was tested by eighteen input data and five output data. For each data, the predicted values of electrochemical properties were compared with mean error percentage (MRE) and root mean squared (RMS). MRE and RMS were defined as follows respectively:

$$RMS = (1/p) \Sigma |V_e - V_p|^2)^{1/2},$$

(15)

$$MRE = (1/p) |(V_e - V_p)/V_e| \times 100\%,$$

(16)

where $p$ is the number of experimental data, $V_e$ is the experimental value of electrochemical properties, and $V_p$ is the predicted value of electrochemical properties.
7 Results and Discussion

Comparison of experimental data and prediction data of train set were shown in Figure 4 when training MSE was 0.001. It showed that improved PSO-BPNN model were characterized by high training precision and well fitting prediction result (experimental data represented by “·” and prediction data represented by “+”).

![Figure 4: Comparison of experimental and predicted data of train set](image)

Generalization ability is used to verify if the prediction data of test set and experimental data fit very well. The generalization ability of the system is more important. By comparing the prediction data with experimental data of test set, it could be clearly seen that experimental data were very close to the predicted data of test set from Figures 5 and 6.

RMS and MRE of train and test sets were shown in Table 3. It can also be realized that the PSO-BPNN model characterize perfect prediction and generalization performances.

<table>
<thead>
<tr>
<th>$S_{BET}$</th>
<th>RMS-train</th>
<th>MRE-train</th>
<th>RMS-test</th>
<th>MRE-test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0018</td>
<td>0.0021</td>
<td>0.052</td>
<td>0.0102</td>
</tr>
<tr>
<td>Specific capacitance</td>
<td>0.0024</td>
<td>0.0023</td>
<td>0.065</td>
<td>0.0322</td>
</tr>
</tbody>
</table>

Before this study, activated carbon EDLCs’ electrochemical properties prediction
model based on BPNN had been established. To further verify the accuracy of the PSO-BPNN model, we compared the prediction results of BPNN model with the results of PSO-BPNN model. The comparison results were shown in Table 4.

It can be seen from the Table 4 that BPNN model did enough to meet a requirement for predicting application of activated carbon EDLCs’ electrochemical properties, but the largest relative error percentage of BPNN model is more 5.5% than that of improved PSO-BPNN model and the average relative error percentage is more 5% than that of improved PSO-BPNN model. In the light of the maximum, minimum, RMS or average errors, the PSO-BPNN’s are all less than BPNN’s. In addition, during training and testing process, execution time of PSO-BPNN is quicker 3.4 times than BPNN’s. It is clear that the prediction and generalization perfor-
<table>
<thead>
<tr>
<th>NO.</th>
<th>Experimental data</th>
<th>BP NN model</th>
<th>Advanced PSO-BP NN model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Predicted value</td>
<td>MRE</td>
<td>Predicted value</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BET</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific capacitance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>3013</td>
<td>2985</td>
<td>2993</td>
</tr>
<tr>
<td></td>
<td>284</td>
<td>276</td>
<td>2750</td>
</tr>
<tr>
<td>B2</td>
<td>2663</td>
<td>2631</td>
<td>2750</td>
</tr>
<tr>
<td></td>
<td>271</td>
<td>224</td>
<td>2562</td>
</tr>
<tr>
<td>B3</td>
<td>2559</td>
<td>2514</td>
<td>2562</td>
</tr>
<tr>
<td></td>
<td>226</td>
<td>220</td>
<td>2719</td>
</tr>
<tr>
<td>B4</td>
<td>2169</td>
<td>2126</td>
<td>2719</td>
</tr>
<tr>
<td></td>
<td>219</td>
<td>225</td>
<td>2181</td>
</tr>
<tr>
<td>B5</td>
<td>2772</td>
<td>2704</td>
<td>2704</td>
</tr>
<tr>
<td></td>
<td>245</td>
<td>0.0066</td>
<td>0.0066</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.00176</td>
<td>0.00176</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.052</td>
<td>0.052</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.065</td>
<td>0.065</td>
</tr>
<tr>
<td>RMS</td>
<td></td>
<td>0.087</td>
<td>0.087</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.093</td>
<td>0.093</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.052</td>
<td>0.052</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.065</td>
<td>0.065</td>
</tr>
</tbody>
</table>

Table 4: Comparison results of BP NN and improved PSO-BP NN.
The aim of this paper was to show material chemometrics and NNs intelligent theory application possibility for the activated carbon EDLCs’ electrochemical properties. Results show that the NNs can be used as an alternative theoretic method in material systems. In this work, the electrochemical properties prediction model was developed and optimized using improved PSO BPNN algorithm. Based on experimentation and investigation carried out, the following conclusions are drawn:

a. NN model with three layers and one hidden layer of 6 neurons is a powerful method for predicting activated carbon EDLCs’ electrochemical properties.

b. The combined improved PSO-BPNN model can be well used to optimize prediction model. The prediction model is characterized by good approximation performance as RMS-test of $S_{BET}$ and RMS–test of specific capacitance are 0.052 and 0.065 respectively. MRE of $S_{BET}$ and specific capacitance between experimental data and the predicted output are 1.02% and 3.22% respectively. Hence, prediction model for activated carbon EDLCs’ electrochemical properties based on improved PSO-BPNN is possessed with good approximation, rapidly converging and high precision.

c. The advanced PSO-BPNN modeling method is simple, rapid and reliable. The essential principle can be popularized to prediction and simulation of other material system.

In addition, by defining more impact factors and more experimental data, the improved PSO-BPNN model would present better prediction and generalization performance, however, this would increase experiment cost and time.

Although PSO-BPNN is an efficient intelligent theory method for activated carbon EDLCs’ electrochemical properties, it should consider more variables of experimental conditions. These extensions will be the focus of our future work.

Acknowledgement: This work was partly supported by National Science Foundation of China (No. 50730003 and No. 50672025), National Project of Scientific and Technical Supporting Programs Funded by Ministry of Science & Technology of China (No. 2007BAE55B00), National High Technology Research and Development Program of China (No. 2007AA05Z311), and Program for New Century Excellent Talents in University (NCET-07-0285).
References


Qu, D.Y.; Shi, H. (1998): Studies of activated carbons used in double layer capaci-


