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Exploration of artificial neural network [ANN] to predict the electrochemical characteristics of lithium-ion cells

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Abstract

CoO anode, as an alternate to the carbonaceous anodes of lithium-ion cells has been prepared and investigated for electrochemical charge–discharge characteristics for about 50 cycles. Artificial neural networks (ANNs), which are useful in estimating battery performance, has been deployed for the first time to forecast and to verify the charge–discharge behavior of lithium-ion cells containing CoO anode for a total of 50 cycles. In this novel approach, ANN that has one input layer with one neuron corresponding to one input variable, viz., cycles [charge–discharge cycles] and a hidden layer consisting of three neurons to produce their outputs to the output layer through a sigmoid function has been selected for the present investigation. The output layer consists of two neurons, representing the charge and discharge capacity, whose activation function is also the sigmoid transfer function. In this ever first attempt to exploit ANN as an effective theoretical tool to understand the charge–discharge characteristics of lithium-ion cells, an excellent agreement between the calculated and observed capacity values was found with CoO anodes with the best fit values corresponding to an error factor of <1%, which is the highlight of the present study.

Keywords: Artificial neural network; Back propagation; Lithium-ion cells; CoO anodes; Charge–discharge cycle

1. Introduction

Batteries are highly non-linear devices for which there are no simple and accurate physical models available to predict the underlying complex phenomena, such as reaction mechanism, charge–discharge behavior, cycle life, capacity retention, etc. Basically, mathematical models of physical systems are constructed to facilitate our understanding of mechanisms that lead to specific responses and to enable response predictions. This creates the need for prediction tools that provide users with useful information such as remaining working time, available energy at every desired time of operation, etc. In this regard, the artificial neural networks (ANNs), one of the most powerful modeling techniques with very quick return for the practice could be explored as a possible tool to predict the charge–discharge characteristics of rechargeable batteries. Because, ANNs play a vital role in analyzing and predicting the behavior of systems that cannot be described by any analytical equations. Towards this direction, the ANNs have been applied to model certain complicated processes related to the field of engineering, viz., aerospace, automotive, electronic, manufacturing, robotics, telecommunication, etc. ANN method is now almost a standard modeling technique based on statistical approach. Particularly, ANN is an inductive or data-based model for the simulation of input/output mappings. One of the distinct characteristics of the ANN is its ability to learn from experience and examples and to get adapted with changing situations accordingly.

In recent years, multivariate methods and ANNs are used to predict the capacity behavior of lead-acid batteries [1–7] alone, wherein literature is replete with reports on the modeling and prediction of characteristics of lead-acid batteries [8]. In this regard, ANNs have been used to predict capacity and power [6,9], gust effects on a grid-interactive wind energy conversion system with battery storage [10], cycle life and failure mechanism of lead-acid system [11]. On the other hand, ANN has been deployed for the first time to understand and to predict possibly the rechargeable lithium-ion cell charge–discharge characteristics through the present study. Since there are no reports on the modeling and prediction of charge–discharge behavior

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of lithium-ion cells, it is aimed through the current study to exploit the same for a lithium-ion system containing CoO anode.

It is well known that the problems associated with the deployment of existing category lithium battery anodes such as graphite/carbonaceous anodes [12], tin-based oxides [13], metal–metal alloys [14], ternary metal borides, silicides and nitrides [15,16], etc., have placed greater emphasis upon the need to identify certain novel/alternate anodes ultimately. As a result, new class of metal oxide [17] and vanadate anodes [18] are being investigated off late and among the variety of 3d-metal oxide anodes, CoO anode has been chosen for the present study, based on our earlier investigation [19]. Further, the experimental results obtained from the charge–discharge analysis of Li/CoO half cells containing an electrolyte made up of 1:1 (v/v) EC:DEC dissolved in 1 M $LiPF_6$ were compared with the predicted values of ANN with a view to understand the possibility of arriving at the best fit values ultimately. Also, the study highlights on the possibility of exploiting ANN technique to predict the charge–discharge capacity values of Li/CoO half cells with the lowest error value (<1%).

1.1. Methodology of modeling/artificial neural network

Artificial neural network modeling is essentially a 'black box' operation linking input to output data using a particular set of non-linear basis functions. ANNs consist of simple synchronous processing elements, which are inspired by biological nervous systems [20] and the basic unit in the ANN is the neuron [21]. ANNs are trained using a large number of input data with corresponding output data (input/output pairs) obtained from actual measurement so that a particular set of inputs produces, as nearly as possible, a specific set of target outputs. Training consists of adjusting the weight associated with each connection (synapse) between neurons until the computed outputs for each set of data inputs are as close as possible to the experimental data outputs. It is well known that during the design and training of ANNs, factors such as (i) architecture of the ANN; (ii) training algorithm; and (iii) transfer function need to be considered eventually.

The term "architecture of the artificial neural network" refers to the number of layers in the ANN and the number of neurons in each layer. In general, it consists of an input layer, one or more hidden layers and one output layer. The number of neurons in the input layer and the output layer are determined by the number of input and output parameters, respectively. In order to find the optimal architecture, number of neurons in the hidden layer has to be determined (this number will be determined based on the ANN during the training process by taking into consideration the convergence rate, mapping accuracy, etc.). The most widely used network type is multi-layered feed-forward network [22,23] trained with the back-propagation learning algorithm [24–34]. The BPN algorithm is based on the selection of a suitable error function, whose values are determined by the actual and predicted outputs of the network. The model with lowest prediction error is being used as the final and optimal model. The activation function of a neuron is defined as the sum of the weighted input signals to that neuron:

$$\mathrm{Net}_j = \Sigma W_{ij} X_i$$

where W_{ij} is the weight-connection to neuron j in the current layer from neuron i in the previous layer and X_i is the input signal of neuron. The Net_j of the weighted inputs is transformed with a sigmoid transfer function, which is used to get the output level. This function is as follows:

$$Y_j = \frac{1}{1 + \mathrm{e}^{-\mathrm{Net}_j}}$$

where y_j is the output of neuron j. Generally, the root mean squared error (RMSE) is used as the error function for finalizing the training and testing process [23]. The goal of training a network is to change the weights between the layers in a direction that minimizes the error E:

$$E = \left[\frac{1}{n(\Sigma_\mathrm{p}\Sigma_\mathrm{k}(y_\mathrm{pk} - t_\mathrm{pk})^2}\right]^{0.5}$$

The error E of network is defined as the squared differences between the target values 't' and the outputs 'y' of the output neurons summed over p training patterns and k output nodes.

With this background, the study deals with the possibility of deploying ANN technique for lithium-ion battery performance prediction, via comparison of predicted and observed specific capacity values of lithium-ion cells containing CoO anodes upon extended charge–discharge cycling process.

2. Experimental method (synthesis of CoO) and method of approach (ANN)

2.1. Preparation of CoO anode

The compound CoO selected for the present investigation was synthesized via thermal decomposition of $CoCO_3$ at 850 °C. A weighed amount of $CoCO_3$ powder was heated inside a tubular furnace at a temperature of 800 °C in an atmosphere of flowing argon. Generally, the synthesis of CoO is reported to associate with common impurities of Co_3O_4 and so the process of high-temperature calcination was carried out under the influence of argon gas flow. Also, the precursor mixture kept inside the furnace was subjected to a process of intermittent grinding at least twice, i.e., at the end of every 6 h, to ensure reaction mixture homogeneity and phase purity of the formed final product. Again, the process of heating was extended for another 3 h, especially to obtain CoO with maximum purity and stability by way of expelling the CO_2 gas completely from the selected carbonate precursor. Also, the post heat treatment after 12 h is expected to exclude the co-existence of trace amounts of cubic Co_3O_4 from the final product thoroughly. The compound CoO obtained as ultra fine powders at the end of 15 h. heat treatment in argon gas flow was subjected further to electrochemical characterization, viz., charge–discharge studies.

The anode electrode was prepared by coating a slurry that contained a mixture of synthesized metal oxide powder (80% by weight), carbon (10%) and PVdF binder (10%) over a copper foil and the details pertinent to the same are mentioned

elsewhere [35] Further, laminated pouch cells of 6 in. × 4 in. dimensions were fabricated and subjected to charge–discharge cycling studies at a constant current (C/10) rate.

2.2. ANN training approach: (software development)

Generally, steps to be followed to develop an ANN model are: (i) database collection; (ii) analysis and pre-processing of the data; (iii) training of the ANN; (iv) test of the trained network; and (v) use of the trained ANN for simulation and prediction. Accordingly, data obtained by experimental measurement of CoO/Li cells were split into two data sets, one of which is a training set and the other is the test set.

In the present ANN model, the input layer has one neuron (charge–discharge cycles), the hidden layer has three neurons (training data selection method) and the output layer has two neurons such as Q_{dc} and Q_c (Q_{dc} = discharge capacity and Q_c = charging capacity). With initial random weight, learning rate and momentum values, preprocessed training data was applied to the BPN network and the optimal number of neurons in the hidden layer was determined. Training was stopped, when the prediction error was found to be the lowest. The objective of the training procedure is to find a set of possible weights that permit the network to estimate/predict the ANN output, in order to minimize the error. ANN model with the lowest prediction error was used as the final and optimum model. Using these optimum values, the network was tested for the unknown (test) data (data not presented to the network during training). The procedure was repeated for different sets of training-test data also and the software for ANN method was developed in Visual Basic.

3. Results and discussion

3.1. Charge–discharge characteristics of CoO anodes in lithium-ion cells (experimental results)

The lithium storage capacity and the cycling efficiency of cobalt oxide electrode was examined through charge–discharge measurements carried out between 0.0 and 3.5 V at a constant current rate of C/10 (Fig. 1). The compound CoO exhibits a capacity of ~300 mAh/g upon first discharge, and a subsequent

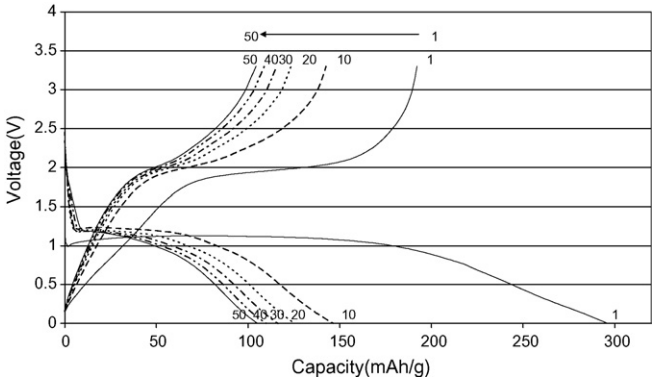

Fig. 1. Charge–discharge behavior of CoO.

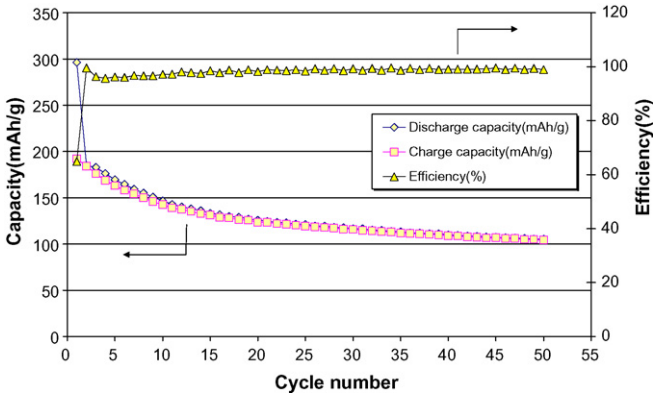

Fig. 2. Cycleability behavior of CoO compound.

capacity fade of <10% up to 50 cycles. The discharge plateau observed around 0.8 V may be attributed to the decomposition of CoO to form metallic Co particles of nano-size, which are dispersed in lithia (Li_2O) matrix. The nano-sized Co and the pseudo-amorphous nature imparted to the CoO matrix during the process of first discharge are believed to be maintained in the following cycling steps also, based on the cycling behavior of CoO anode up to 50 cycles. Thus the compound CoO undergoes a reversible decomposition process and substantiates the observed fairly high capacity values upon extended cycling.

It is already reported [36] that the insertion of lithium causes the local structure around cobalt atoms to become asymmetric, and the small sized Co particles are believed to evolve gradually with a well-separated distribution in the lithia matrix. As a result, during the successive extractions of lithium, the reduced cobalt particles are reported to return reversibly to the high-temperature cubic phase of CoO, thus substantiating the minimum capacity fade of <10% up to 50 cycles. From this, it may be concluded that CoO seems to be a good candidate as far as the magnitude and the retention of specific capacity are concerned. The coulombic efficiency of the synthesized CoO anode is found to be satisfactorily good, as evidenced from Fig. 2 an indication that the oxide material chosen for the present study qualify itself as one of the possible candidates of existing category metal oxide anodes, by way of possessing an appreciable storage capacity for lithium.

3.2. Deployment of ANN technique for cycle life prediction of CoO anode (theoretical values)

Generally, ANNs have the capability to transform and reduce complicated, coupled systems into an inductive framework for mathematical analysis and data-based modeling [37]. To verify the estimation/prediction ability of the ANN models developed (trained), different sets of test data (specific capacity values of charge–discharge cycles) were presented to the network. Subsequently, the estimated and predicted values were compared with the measured specific capacity values, up to 50 charge–discharge cycles. It is quite interesting to note that the estimated and predicted values are in good agreement with the experimental values. Graphs plotted for training and estimated/predicted data for different training data approach are shown in Figs. 3–6.

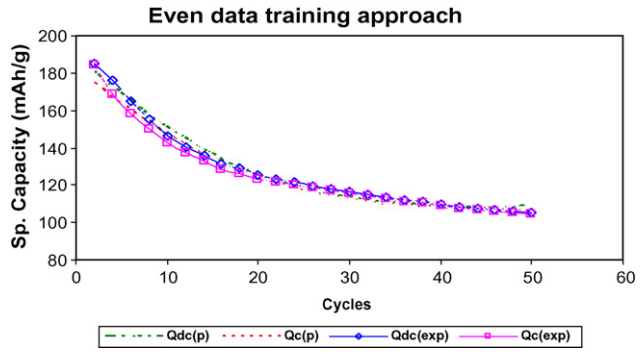

Fig. 3. Estimation (interpolation) of odd cycle charge–discharge behavior—even cycle data training approach.

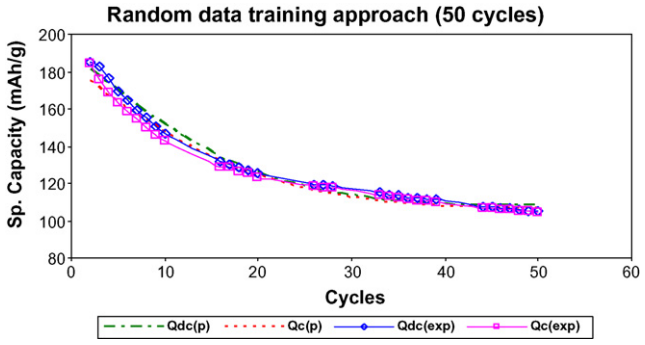

Fig. 4. Estimation (interpolation) of intermediate cycles charge–discharge behavior—random data (up to 50 cycles) training approach.

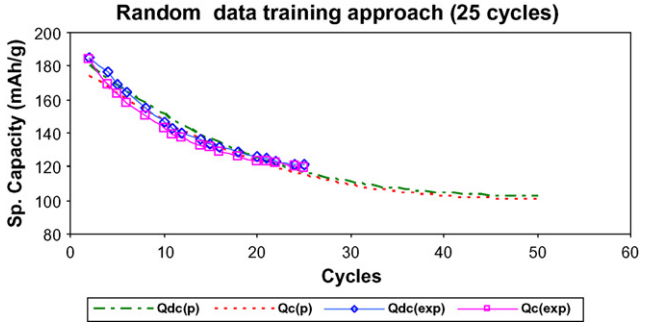

Fig. 5. Prediction (extrapolation) of extended cycle charge–discharge behavior—random data (up to 25 cycles) training approach.

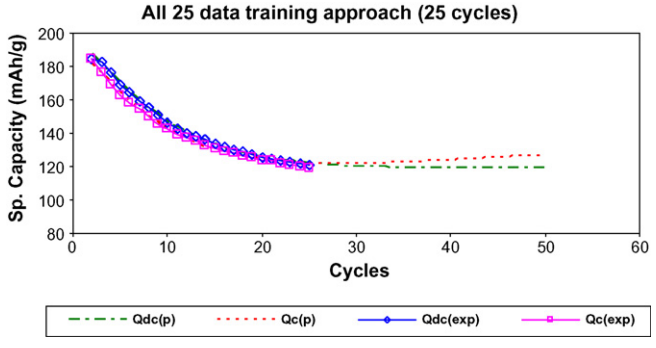

Fig. 6. Prediction (extrapolation) of extended cycle charge–discharge behavior—all 25 data (up to 25 cycles) training approach.

Methods adopted:

Method (estimation (*E*)/prediction (*P*))	Training set	Test set
Estimation	Even cycle data selected from 1 to 50 cycles	Odd cycle data from 1 to 50 cycles
Estimation	Random cycle data selected from 1 to 50 cycles	Remaining cycle data from 1 to 50 cycles
Estimation and prediction	Random cycle data selected from 1 to 25 cycles only	Remaining cycle data up to 50 cycles
Prediction	All 25 cycles data (up to 25 cycles)	Remaining cycle data (26–50 cycles)

In other words, Fig. 3 shows the estimation (interpolation) of odd cycle charge–discharge behavior for even cycle training data approach, which is a commonly reported methodology in the literature [7,38]. On the other hand, estimation (interpolation) of in-between cycles for charge–discharge behavior for random data training approach (up to 50 cycles) is a newer approach and the results pertaining to the same are furnished in Fig. 4. Similarly, prediction (*extrapolation*) of data for a total of 50 cycles for charge–discharge behavior for random data training approach (up to 25 cycles) and the prediction (*extrapolation*) of data for a total of 50 cycles for charge–discharge behavior for all the consecutive 25 cycles training data approach are depicted in Figs. 5 and 6, respectively. Herein, it is worth mentioning that literature has no reports on the training of random cycle data so also the extrapolation of data, based on chosen category training imparted to the system. To be more precise in authenticating the ANN approach to estimate/predict the charge–discharge values of lithium-ion cells containing CoO anodes, the selection of random data testing and the extrapolation of the same for random data as well as for all the 50 cycles data were made, which is the significance of the present study.

Further, Figs. 7 and 8 show the graphs plotted for experimental versus estimated/predicted data for different training data approach with the best fit values (correlation coefficient). It is obvious from all the figures that an excellent agreement between the experimental and estimated/predicted capacity values are observed, an indication that ANN models can also be used for extrapolation of data with some extended range. This is an interesting observation, since literature reports that ANNs are not

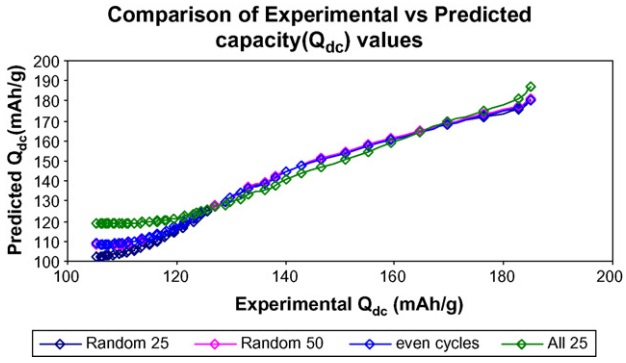

Fig. 7. Experimental vs. predicted values (Q_{dc}).

Table 1
Error values obtained for the different training data approach

Training data approach	RMSE	Correlation coefficient		Hidden layer neurodes
		Q_{dc}	Q_c	
Even cycles (*E*)	0.0081436	0.9837	0.9783	3
Random 50 (*E*)	0.0080256	0.9841	0.9785	3
Random 25 (*E* and *P*)	0.0027328	0.9797	0.9731	3
All 25 (*P*)	0.0099867	0.965	0.8747	3

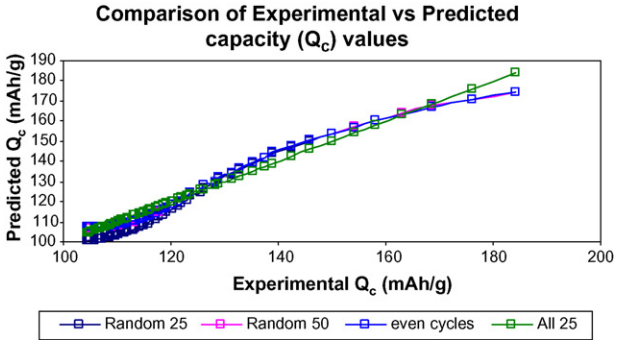

Fig. 8. Experimental vs. predicted values (Q_c).

usually good extrapolators [9]. However, the present study has paved way for the exploitation of ANNs to extrapolate the data also as investigated and verified with the CoO anodes deployed in lithium-ion cells.

Similarly, the error values obtained for the different methods of training data approach are displayed in Table 1, which is well within the permissible level (<1%). As it is seen from figures and table, the estimation/prediction data has a good compatibility with the corresponding experimental data, thus leads to the best fit correlation coefficient (r>0.90). In particular, the random data training (up to 50 cycles) approach has encountered the highest value [r = 0.9841 (Q_{dc}); r = 0.9785 (Q_c)], compared to the rest of the training data approaches. Thus, it is explicit that the proposed ANN model has demonstrated high degree of accuracy and the possibility of estimation of the charge–discharge behavior of lithium-ion cells containing CoO anode.

4. Conclusion

The compound CoO has been synthesized in its pure form, without the possible co-existence of Co_3O_4 impurities by adopting a carefully monitored solid-state synthesis methodology. The compound, due to its phase purity and better crystallinity exhibited a capacity of ~300 mAh/g, without much capacity fade up to 50 charge–discharge cycles. Further, estimation/prediction and verification of specific capacity values as a function of cycle life has been made using ANN with a selection of even data and random data (up to 50 cycles) for interpolation of results and all data pertaining to 25 cycles (all 25 cycles) and random data among 25 cycles for extrapolation (up to 50 cycles) of results. Interestingly, an excellent agreement between the experimental and estimated/predicted capacity values were observed for all kinds of chosen category ANN training data approach, with a special relevance to the random 50 cycles training data approach with a correlation coefficient of ~0.98. Thus, it is demonstrated that ANN could be deployed as an effective theoretical tool to estimate/predict the cycle life characteristics of Li-ion cell with CoO anodes. As an extension of this work, studies on the prediction of extended cycle life performance behavior of variety of alternate anodes deployed in lithium-ion cells using ANN technique are underway.

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