

A modified cellular automaton model for simulating ion dynamics in a Li-ion battery electrode

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ABSTRACT

Lithium-ion batteries are the dominant energy storage tools for electric vehicles and portable devices. Their prospects depend on the development of new electrode materials. The electrode properties are highly affected by phenomena on the electrode's surfaces. Besides experimental means, there are various simulation ways to investigate these phenomena where experiments have difficulty analyzing. However, simulating some of these events is challenging for existing simulation methods, and researchers are looking for new simulation tools to fill this gap. Here, we focus on developing and evaluating a new method for studying the key surface phenomenon inside a battery electrode in nanoscale, i.e., adsorption. In particular, we are interested in the adsorption behavior of ions on the surface of a nanosized electrode. We developed a general cellular automata model for studying the adsorption behavior of various materials, where desorption and intercalation happen during an adsorption process. The model results are compared with Freundlich isotherm and show a high resemblance. Also, an experiment concerning the lithium-ion adsorption on Titania nanotube is modeled with our C.A. model. The model is highly time-efficient and exhibits spectacular performance for simulating relatively complex systems as the results are quite close to the experimental results. As this model is general, its local rules and parameters can be modified and calibrated easily with either experiment or simulation, enabling one to study various sorption behaviors.

Keywords: Lithium-Ion Battery, Adsorption, Cellular Automaton, Freundlich Isotherm.

1. Introduction

Lithium-Ion Batteries (LIBs) were first commercialized in 1991 and drawn much attention due to their outstanding properties such as low self-discharge, high cyclability, and high working voltage [1]. Although the LIBs have improved drastically since their introduction, the need for higher charge capacity and charging rates remains. The battery's performance is largely determined by the electrode's materials [2]. Researchers need

to examine materials' properties and modify them to achieve the intended characteristics. In contrast to experimental investigations, computer-based simulation of LIBs offers a low-cost and relatively fast means for examining materials' properties. The simulations' credibility relies on accurate and efficient simulation methods of batteries electrode phenomena, which are; 1. Adsorption 2. Intercalation 3. Desorption [3]. The behavior of an adsorption system can be reported through an adsorption isotherm. Each isotherm has a specific set of assumptions; therefore, the material properties can be determined by

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examining their corresponding adsorption isotherm. In other words, having a model able to produce accurate adsorption isotherms would mean the model has the right assumptions about the materials' properties.

There are various ways to model adsorption phenomena, namely; Density Functional Theory (DFT), Finite Element Method (FEM) simulation, and molecular dynamics (M.D.). While these methods play a major role in modeling various battery phenomena[4], modeling some events like desorption and intercalation of lithium-ions is quite challenging as the timescale of these phenomena are usually much larger than the current computational potential of these methods[5-7]. Therefore, researchers are inclined to develop methods such as Cellular Automata (C.A.), which can simulate these phenomena for a system.

Cellular Automata (C.A.) is an algorithm that describes the discrete spatial evolution of complex systems by defining local or global deterministic or probabilistic transition formation rules to the cells of a lattice, which typically has arbitrary dimensions[8]. The evolution of a C.A. model takes place by applying certain transition rules that affect the state of each cell. The rules determine the state of a site based on its previous state and the state of the neighboring cells (local rules) or the state of all cells(global rules)[8]. Due to their simplicity, C.A. simulation models exhibit high-speed capacity.

There are similar methods known as Lattice Gas Cellular Automata (LGCA) and lattice Boltzmann models, which can simulate flow with high accuracy, e.g., they can derive Navier-Stokes equations for a system[9]. However, these models are relatively complex compared to C.A. models and computationally costly[10]. Moreover, a classical C.A. model local rules are intuitive and easy to modify based on one's perception of an event. Focusing on the adsorbent surface, C.A. models have been employed to simulate adsorption [10, 11]. These models did not consider free-moving particles, and no comparison was made with an adsorption isotherm. Besides, the lattice Boltzmann model has also been used to simulate various adsorption isotherms[12]; however, the complexity of this model is relatively high, and

the use of this model requires a sound understanding of its theoretical principles.

In this work, we developed a classical-probabilistic C.A. model where adsorption of free-moving particles occurs on an adsorbent, followed by their desorption and intercalation. The model's ability is verified through a comparison of the results with the Freundlich isotherm. Our model's advantage is that the local rules are intuitive and easy to modify for adsorbate and adsorbent, enabling one to model a wide range of materials and conditions, e.g., temperature effects, interactions, and adsorbent pore sizes.

2.Model

The model aims at predicting the equilibrium surface coverage (θ) of an adsorbent, where:

$$\theta = \frac{\text{Number of adsorbed particles}}{\text{Number of adsorption sites}} \quad (1)$$

All phenomena occur inside a simulation box, containing two types of particles: free moving and adsorbed on an adsorbent surface. The adsorbent surface can represent an electrode in a battery, and the adsorbate can be deemed Li-ions. Since this is a probabilistic C.A. model, anything that could happen is associated with a probability number.

The simulation box has a cellular pattern with a cell size equal to 1. Each cell's state is either 1(occupied cell) or 0 (empty cell). The adsorbent surface is located at the $Z=0$ plane, and periodic boundary conditions are imposed in x and y directions. The top plane of the box acts as a hard wall, so when a particle strikes that plane, it reverses its moving direction in the z -direction, maintaining its velocity magnitude, i.e., perfect elastic impact. In addition, the box has a larger length in z -direction compared to the other two directions so that a small fraction of the moving particles would be adsorbed; thus, the concentration of the moving particles can be assumed constant.

In the initial time step, several particles are generated and dispersed randomly throughout the box (Fig.1). The number of these particles is about the concentration of adsorbate particles, defined beforehand. Each particle is assigned a velocity according to the Maxwell-Boltzmann distribution[13]. For each axial direction, a

random number is produced for each particle that shows the probability of movement in that direction. Its sign indicates the positive or negative direction of motion, and its magnitude determines the particle's velocity magnitude. The magnitudes are normalized to have a meaningful probability value. Therefore, the generated random numbers are divided by 3, and those with an absolute value larger than 1 are set equal to 1. These particles are free to move until they collide with the adsorbent. The system evolution is done by comparing the velocity of each particle with a randomly

generated number. Suppose the random number is less than the magnitude of the velocity in a specified direction. In that case, the particle will move to the adjacent cell based on the velocity direction. During evolution, periodic boundary conditions along the x and y directions are applied, i.e., particles exiting the box enter the box on the opposite side. In addition, the Moore neighborhood is assumed for the movement of the particles so that the particles can move in all their neighbors (Fig.2). At the first timestep, the adsorbent is unoccupied, and it fills by adsorbing impacting particles (Fig.3).

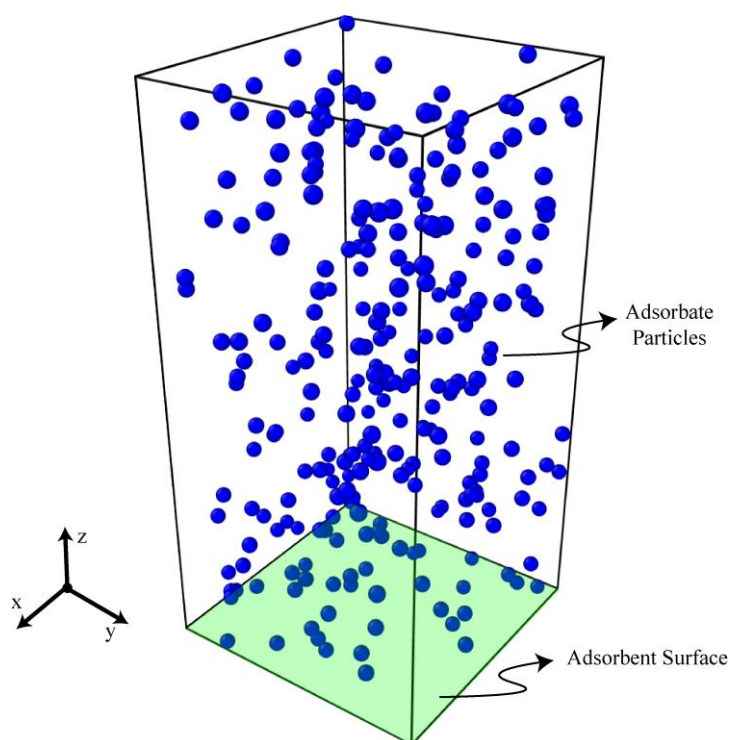


Fig. 1. Simulation box and the particles

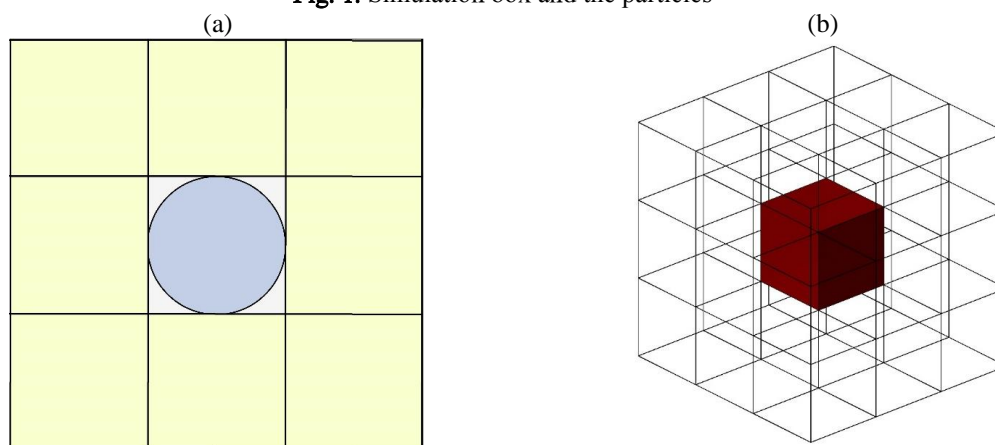


Fig.2. (a) 2D and (b) 3D Moore neighborhood

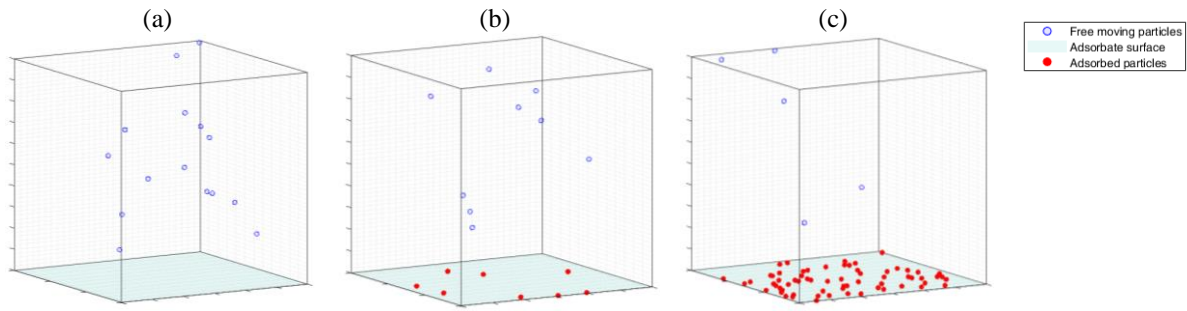


Fig.3. From (a) to (c), time evolves, and the adsorbent surface coverage is increased until reaching equilibrium

There are two scenarios when a free-moving particle hits the adsorbent surface: either the site is full or empty. The particles hitting an empty site are adsorbed with a definite probability (P_{Ads}). An adsorbed particle may desorb from the surface based on its probability (P_{Des}). On the other hand, when a particle strikes a full site, two events may occur, which are based on a predefined probability:

1. The particle may get adsorbed.
2. The particle may return to space ($P_{Bounce} = 1 - P_{Ads}$).

For the first event, the adsorption probability of that site is multiplied by a decreasing coefficient (Ads_{coef}), while the desorption probability is multiplied by an increasing coefficient (Des_{coef}). An Ads_{coef} with a value less than 1 can simulate a case where the adsorption energy increases when surface coverage is increased, meaning there is repulsion interaction among adsorbate-adsorbate. Conversely, the Ads_{coef} with a larger value of 1 means attraction among adsorbates and simulates a decreasing adsorption energy barrier; more information on the adsorbate interaction and adsorption energy can be found in the literature[14]. The adsorption of another particle in an already occupied site can simulate the intercalation of particles into the bulk of adsorbate, considering the fact that a decaying adsorption probability limits the number of intercalated particles.

3. Results and discussion

In this section, the results of the simulation with the C.A. model will be reported. Since the model is probabilistic, the boundary conditions have some effects on the results. Therefore, the

box dimensions should be large enough to minimize the effects. The first task is to choose the box size. Then from the equilibrium data, the surface coverage for various concentrations of adsorbates is then measured from the equilibrium data, and its resulting isotherm is compared with the Freundlich isotherm.

3.1. Box size

For a set of parameters, the adsorbent's equilibrium surface coverage is measured. For each set of values, ten independent simulations are carried out to obtain statistically reliable results. For example, the degree of coverage for a box size of (100,60) and an initial particle concentration of 1% is illustrated in Fig.4. All curves have approximately the same initial slope before reaching equilibrium. Then they start to oscillate about the equilibrium value. For the degree of coverage calculation, a relaxation time is defined. We have chosen 2500 steps for relaxation time, and the degree of coverage for each simulation is averaged after this relaxation time.

The average and the Relative Standard Deviation (RSD) of the degree of coverage for different box sizes can be observed in Fig.5. From this figure, it can be interpreted that the surface coverage converges about 45% by increasing the sizes. Also, by increasing the size in the X and Y axis, the standard deviation reduces. However, increasing the size comes with a high computational cost. Therefore, the size ($L_x = L_y = 60, L_z = 100$) is considered for the box, where the RSD is about 0.009. Henceforth, the degree of coverage does not depend on the box size.

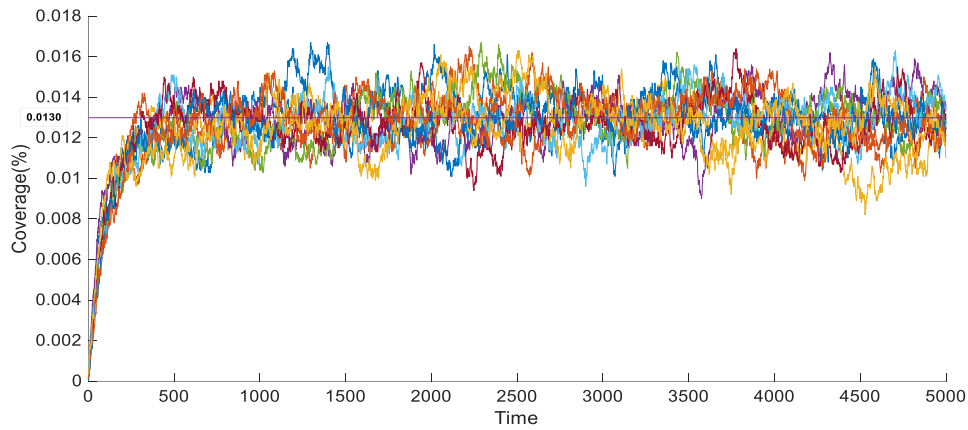
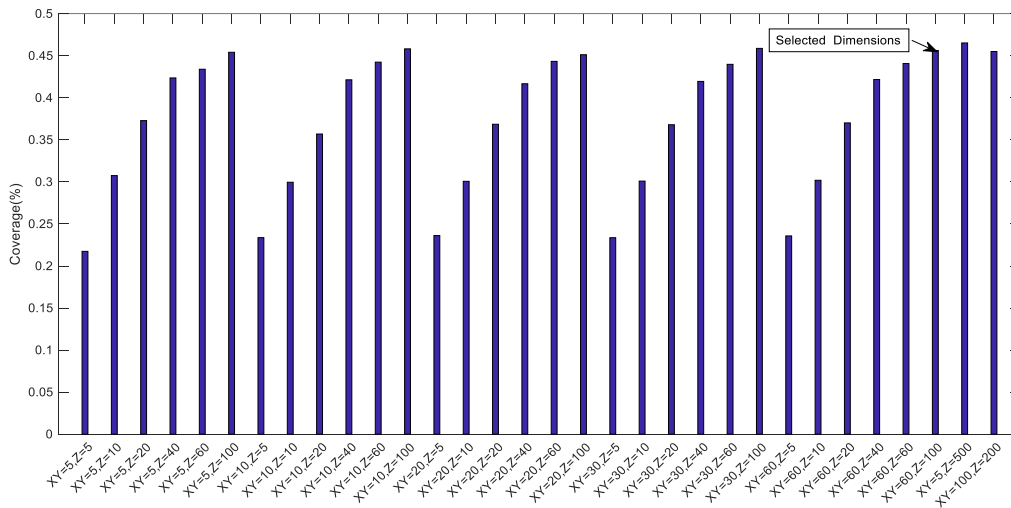


Fig. 4. Degree of coverage through time. Each colored curve shows an independent simulation. (Box size (100,60), Concentration=1%, $P_{Ads} = 0.1$, $Ad_{coef} = 0.9$, $P_{Des} = 0.01$, $Des_{coef} = 1.01$).

(a)



(b)

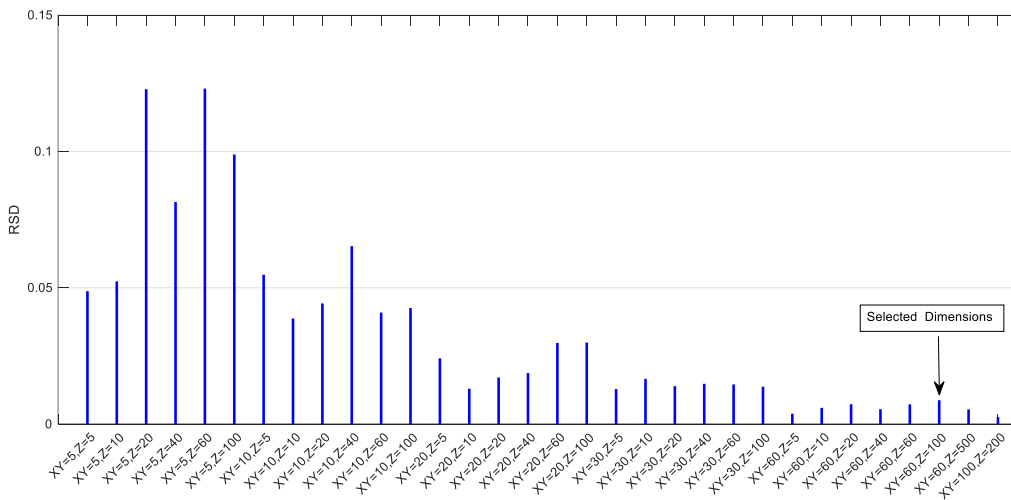


Fig.5. Simulation box size vs. degree of coverage for a certain set of parameters. In the horizontal axis, the first number denotes the length in X and Y-directions, and the second number shows the size of the box in the Z-direction.

3.2.The Model results

Freundlich isotherm is used to evaluate the C.A. model data. The Freundlich isotherm is one of the earliest isotherms with an empirical approach[15]. The Freundlich isotherm can be applied to a variety of problems[16-18]. This isotherm states that the amount of the adsorbed substance a is related to the applied pressure/concentration P by[19, 20]:

$$a = kp^n \tag{2}$$

Where k and n are constants.

The Freundlich isotherm is empirical and does not have clear assumptions[15]. Still, considering the applicability of this isotherm to

certain conditions, it can be interpreted that our model assumptions are following the Freundlich isotherm. The C.A. model results in the data in Fig.6. The comparison of the simulation model with Eq.(1) shows a high resemblance. The goodness of fit is very high as the R-square equals 0.9993. The test is done with the parameters ($P_{Ads} = 0.1, Ads_{coef} = 0.8, P_{Des} = 0.01, Des_{coef} = 1.04$).

The effect of parameters on the results is shown in Fig.7. From Fig.7, it can be interpreted that the P_{Ads} and P_{Des} has a high impact on the results since where other parameters are the same, the degree of coverage varies significantly with changing these parameters.

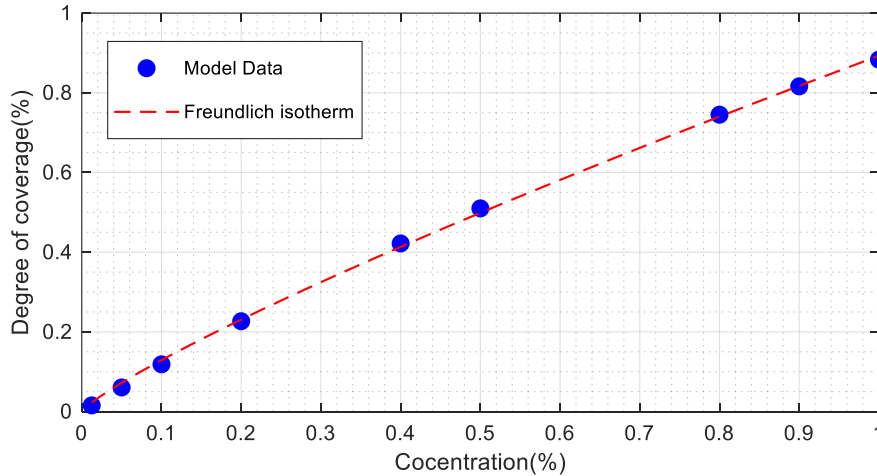
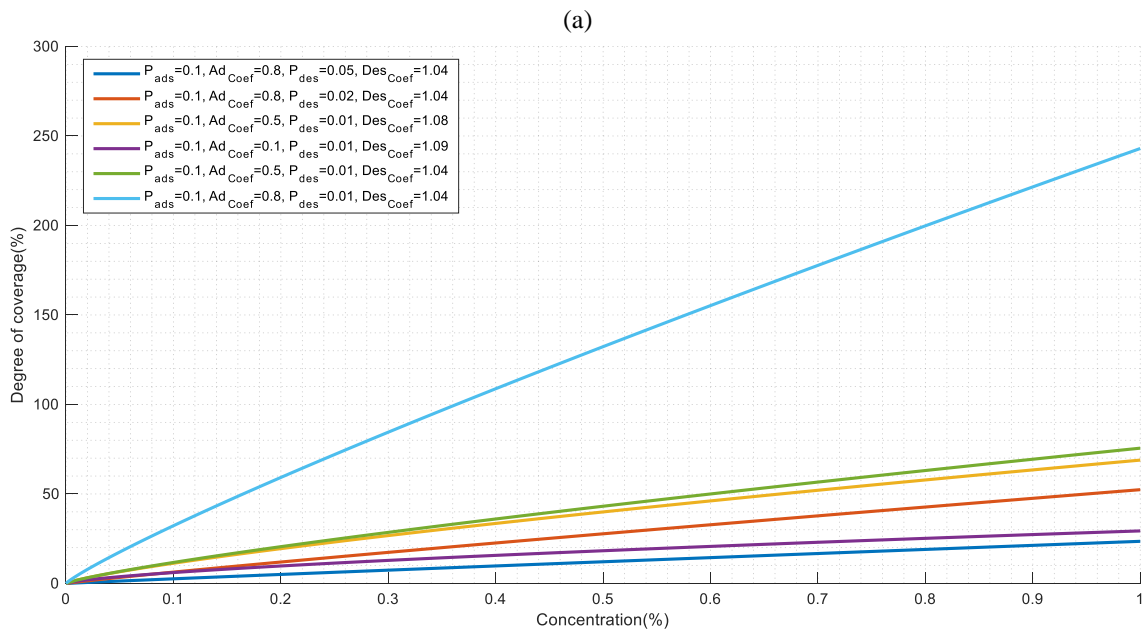


Fig.6. Freundlich isotherm curve fitted on the C.A. model data



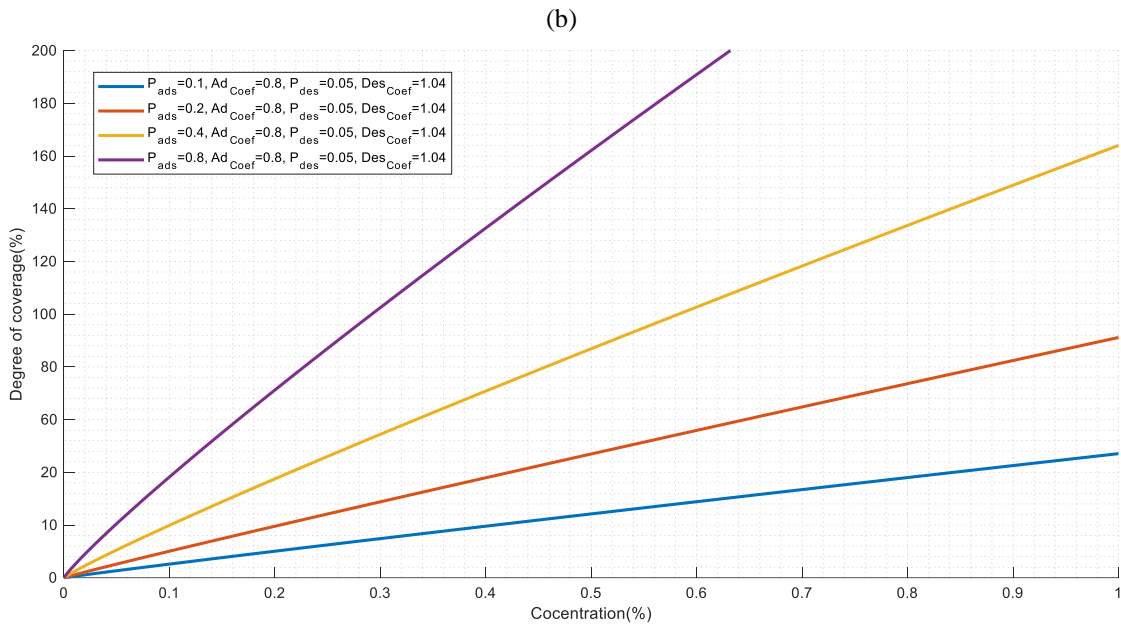


Fig.7. Effect of model parameters on the resulting isotherm.

(a) the adsorption probability is constant. (b) only the adsorption probability is varied.

4.Example: Li-ion adsorption on Titania nanotube

Here we aim to simulate the adsorption of lithium ions on TiO₂ nanotube. Titania is widely used for electrodes. Also, the titania nanotube has the most surface area than all other morphologies, meaning more lithium adsorption sites[21, 22]. Therefore, this material is a suitable material for a battery electrode.

Taghvaei et al. [23] experimentally investigated the lithium adsorption behavior on TiO₂ nanotube. Our C.A. model can simulate their adsorption isotherm with high accuracy (Fig.8). The isotherm parameters for the experiment are $n=1.22$, $K=2.72$. Our model isotherm parameters are $n=1.28$, $K=2.72$ for $P_{Ads} = 0.8, Ads_{Coef} = 0.95, P_{Des} = 0.017, Des_{Coef} = 1.05$.

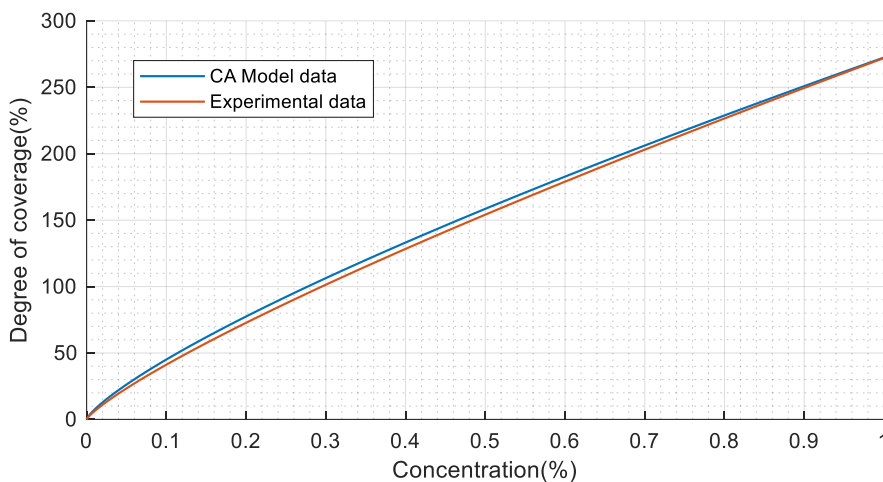


Fig.8. Adsorption Isotherm of Li-Ion on the Surface of Titania nanotube.

5. Conclusion

In this work, we developed a novel probabilistic C.A. model to study the intercalation of lithium ions into an electrode surface during an adsorption process. The Freundlich adsorption isotherm is simulated with high accuracy and speed with a proper definition of local rules. The model's ability to simulate real-world scenarios is pointed out by comparing its results with experimental data. By modifying the local rules and parameters, several different scenarios can be simulated by this C.A. model. The model parameters can affect the equilibrium surface coverage; thus, the model needs proper calibration according to the test conditions. Any local rule should be developed to represent the intended phenomenon properly, and the parameters can be derived from either experiments or simulations. Regarding its decent performance for simulating lithium adsorption on TiO₂ nanotubes, this model can serve as a new tool for researchers working on LIBs.

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