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Article

Keywords: constant potential method (CPM), supercapacitors, molecular modeling

Posted Date: May 27th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-488710/v1>

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Version of Record: A version of this preprint was published at Nature Computational Science on November 22nd, 2021. See the published version at <https://doi.org/10.1038/s43588-021-00153-5>.

Modeling galvanostatic charge-discharge of nanoporous supercapacitors

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Molecular modeling can study the energy storage of supercapacitors at the atomistic level and has become indispensable in this research. The constant potential method (CPM) allows keeping the electric potential uniform on the electrode, which is essential for a realistic description of the charge repartition and dynamics process in supercapacitors. Prior CPM studies have been limited to the potentiostatic mode. Though widely adopted in the experiment, the galvanostatic mode has been rarely investigated in CPM simulations due to a lack of effective methods. In this work, we developed a modeling approach to simulating the galvanostatic charge-discharge of supercapacitors under constant potential (GCD-CPM). We show that, for nanoporous electrodes, GCD-CPM can capture supercapacitor dynamics in excellent agreement with experimental measurements and delineate the ion adsorption-desorption dynamics underlying the hysteresis with molecular resolutions during charging and discharging. Therefore, this GCD-CPM modeling could open up new avenues for exploring the rich physics and electrochemistry of supercapacitor dynamics.

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Supercapacitors have been attracting significant attention due to their high power density and superior cycle time^{1,2}. Researchers frequently resort to molecular modeling to investigate the thermodynamics and dynamics of the energy storage in supercapacitors, particularly those with nanoporous electrodes, because molecular simulations can provide a precise microscopic picture of electric double layers (EDLs) and their formation in supercapacitors³⁻⁵. In the molecular modeling of supercapacitors, how to describe electrode polarization is a critical issue. The most straightforward way is to distribute charges uniformly on electrode atoms (*i.e.*, constant charge method, CCM)⁴⁻⁷. In contrast, the constant potential method (CPM), a computationally expensive but realistic approach, maintains electrode atoms at constant potential, adjusting the electrode charges self-consistently based on the electrode potential and ionic environment⁸⁻¹⁵. To explore the equilibrium performance of supercapacitors, CCM may be feasible for systems with open electrodes (*e.g.*, those with planar¹⁶, cylindrical⁷, spherical¹⁷ surfaces), but not for porous electrodes^{11-13, 18, 19}. To model the charging and discharging process of supercapacitors, CPM is desired because CCM will produce incorrect charging dynamics and heat generation^{19, 20}.

In studying charging and discharging supercapacitors, prior CPM simulations often adopted the potential control mode: step-like,⁸⁻¹⁵ linear,²¹ or climbing-type^{22, 23} potential differences were applied between the positive and negative electrodes. These molecular simulations help to understand the fundamentals of charging and discharging supercapacitors. However, they cannot offer insights into the charging kinetics in the galvanostatic mode that has been widely used in practical applications^{24, 25} and fundamental electrochemical studies (*e.g.*, galvanostatic charge-discharge, GCD)²⁶⁻²⁸. Therefore, modeling the charging and discharging of supercapacitors by regulating electric current and keeping electrode equipotential is highly desirable. Nevertheless, very few such studies are reported due to a lack of effective simulation methods. An approach combining finite electric displacement and constant potential technique was developed very recently but has been demonstrated so far for open electrode systems²⁹. As such, existing GCD simulations were based on CCM, in which charges on electrode atoms were varied linearly and uniformly (in the following, this method is termed GCD-CCM)^{30, 31}.

Herein taking inspiration from previous CPM studies^{8, 9, 13, 15}, we develop a method to model the galvanostatic charge-discharge of supercapacitors under constant potential, rigorously making electrode equipotential at each time step (named GCD-CPM, see Methods). Both GCD-CPM and GCD-CCM have been applied to two typical molecular dynamics (MD) systems of supercapacitors with open electrodes (Fig. 1a) and nanoporous electrodes (Fig. 1b). The ionic liquid ethyl-3-methyl-imidazolium tetrafluoroborate ([EMIM][BF₄]) is used in both systems (Fig. 1c). After equilibrating the simulation under the potential of zero surface charge, we apply a square-wave current with an amplitude of I_0 and a period of P (Fig. 1d) (see Methods). We then analyze the time evolution of the electrode potential and EDL formation in both systems and demonstrate the effectiveness of GCD-CPM via experimental validation.

Fig. 1 | Molecular simulations of the galvanostatic charge-discharge of supercapacitors. a-b, Snapshots of supercapacitors featuring open electrodes (a) and nanoporous electrodes (b). **c,** Coarse-grained models of the ionic liquid [EMIM][BF₄] used in supercapacitors. **d,** The applied electric current of galvanostatic charge-discharge.

Results

GCD-CPM and GCD-CCM produces very similar results for open electrode systems

We first study the open electrode system. Like the GCD test in experiments, MD simulation systems are charged and discharged with a square-wave current for 30 cycles. Figure 2 shows modeling-obtained GCD of the stable cycle with a period of 100 ps (see Supplementary Part 1 for details). In molecular modeling with GCD-CPM, the charges distributed on electrode atoms are not homogenous at *any* instant (Fig. 2a), owing to the thermal motion of electrolyte

molecules^{5, 32}, which is in line with previous works using CPM with step-like potentials^{4, 5, 32}. Such heterogeneity can be quantified by the probability distribution of charges on electrode atoms^{5, 32}. Corresponding to the applied current (Fig. 1d), such probability distributions are analyzed from GCD-CPM simulations for each time step during the charging-discharging process (see Supplementary Part 2 for detailed probability distribution calculation). They are in a volcano-like shape, and their width (or variance) changes a little with time (Fig. 2b for the positive electrode and Supplementary Fig. 2a for the negative electrode). On the electrolyte side, cations and anions, driven by the electrode polarization, form dynamic EDLs, which are delineated by the ion number density as a function of time and distance from the electrode surface (Fig. 2c and Supplementary Fig. 3-4). One can see that EDLs have typical layering structures, consistent with previous observations^{4, 33-35}. During the charging process (0 ~ 50 ps), the first cation layer decreases with time and is slightly away from the electrode surface, while this trend is reversed during discharging (50 ~ 100 ps).

Fig. 2 | Galvanostatic charge-discharge of open electrode systems. **a-c**, GCD-CPM modeling: A snapshot of the positive electrode at 50 ps, with atoms colored by their instantaneous charges (**a**); Gray contour presents probability distributions of electrode charges varying with time, and the dashed line is the average (**b**); Evolution of ion number density with time and distance from the electrode (**c**). **d-f**, GCD-CCM modeling: A snapshot of the positive electrode at 50 ps, with atoms colored by their instantaneous potential (**d**); Gray contour indicates probability distributions of electrode potentials, and the red dashed line is the average (**e**); Evolution of cation number density (**f**). The solid green line in (**e**) is the electrode potential obtained by GCD-CPM.

The galvanostatic charge-discharge of the open electrode system is also explored using GCD-CCM. Instead of calculating charges distributed on electrode atoms at each time step in GCD-CPM modeling, the charge on each electrode atom is preset with the same value in GCD-CCM modeling. The electrode potential is computed accordingly, showing a distinctly heterogeneous distribution (Fig. 2d). However, the averaged potential on the electrode at each time closely matches that by GCD-CPM (Fig. 2e and Supplementary Fig. 2b). Evolution of cation density at the positive electrode computed by GCD-CCM is also found to be nearly the same as that by GCD-CPM (Fig. 2f vs. 2c); comparison of more dynamic EDL structures reaches the same agreement (Supplementary Fig. 3-4). With further checking the ion orientation, the angular distributions of cations adsorbed on the negative electrode obtained by these two methods are almost the same (Supplementary Fig. 5). For additional electric currents in different amplitudes and periods, the results obtained by these two methods again come to the same conclusion (Extended Data Fig. 1).

GCD-CPM is indispensable for nanoporous electrode systems

We then investigate the galvanostatic charge-discharge of nanoporous electrode systems. In GCD-CPM modeling, the probability distributions of electrode charges are in more substantial heterogeneity and vary with time more distinctively (Fig. 3a and Supplementary Fig. 6a), compared with open electrode systems (Fig. 2b and Supplementary Fig. 2a). It could be ascribed to the non-uniform distribution of electrode charges along the pore axis (Extended Data Fig. 2a). In particular, the variation of surface charges at the pore entrance is more extensive than those in the central portion of the pore. Driven by the electrode polarization, the in-pore charge density ρ_e , stemming from the electrolyte, exhibits a similar trend with the varied electrode charges (Fig. 3b vs. Extended Data Fig. 2a).

The potential distributions on nanoporous electrodes were examined via GCD-CCM (Fig. 3c and Supplementary Fig. 6b), compared to GCD-CPM. It can be found that the potential is more heterogeneous than that on the open electrode, and its average differs from GCD-CPM. Remarkably, there is a parabolic-like distribution of the electrode potential from

the entrance to the central portion of a pore (Extended Data Fig. 2b), which conflicts with the fact that the electrode is equipotential. For GCD-CCM, the in-pore charges, driven by the uniformly distributed electrode charges, are less heterogeneous than those obtained using GCD-CPM (Fig. 3d vs. 3b).

Fig. 3 | GCD-CPM and GCD-CCM modeling of galvanostatic charge-discharge in nanoporous electrode systems. **a**, Gray contour indicates probability distributions of atom charges on the positive electrode, obtained from GCD-CPM simulations; the dashed line is the average of such charges. **b**, Evolution of in-pore charge density from electrolyte along the pore ($z = 0$ is the pore entrance), obtained from GCD-CPM simulations. **c**, Gray contour indicates probability distributions of potentials on the positive electrode, obtained from GCD-CCM simulations; the red dashed line is the average of potentials; the solid green line is the potential obtained from GCD-CPM simulations. **d**, Evolution of in-pore charge density from the electrolyte, obtained from GCD-CCM simulations. **e**, Effective diffusivity of in-pore electrolyte under the positive polarization. **f**, Heat generation during a galvanostatic charging-discharging cycle. The pore width is 0.67 nm.

Ion transport under nanoconfinement has been found to have a strong correlation with the charging dynamics and power density of porous supercapacitors^{1, 3, 12}. The in-pore ion transport during the charging-discharging process can be evaluated by the effective diffusivity, which is described as¹²

$$\frac{\partial \rho_e}{\partial t} = D_{eff} \frac{\partial \rho_e^2}{\partial z^2}. \quad (1)$$

Using Eq. 1 and the evolution of in-pore charge density (Fig. 3 and Supplementary Fig. 7), the effective diffusivity D_{eff} of electrolyte in positive nanoporous electrodes is calculated and shown in Fig. 3e (see Supplementary Part 5 for calculation details). Using GCD-CPM modeling, the effective diffusivity in the pore of the positive electrode relative to that of bulk electrolyte D_{eff}/D_{bulk} is 52 ($P=200$ ps), 21 ($P=1000$ ps), and 13 ($P=3000$ ps), close to the prior work using CPM with step-like potentials^{12, 36}. For GCD-CCM modeling, D_{eff}/D_{bulk} is 16566 ($P=200$ ps), 2434 ($P=1000$ ps), and 231 ($P=3000$ ps), which is quite larger than that from GCD-CPM. A similar trend is found in the negative nanoporous electrodes (Supplementary Fig. 8-9).

The previous simulation reported that unphysically huge heat would be generated during the charging process by CCM modeling with inputting step-like charges¹⁹. The heat generated during a charging-discharging cycle of nanoporous supercapacitors is calculated as the energy removed from the system by the thermal bath (detail of heat calculation in Methods). Figure 3f and Supplementary Fig. 10 disclose that the heat generated by GCD-CCM is much more massive than that by GCD-CPM. Therefore, GCD-CCM cannot be used for modeling nanoporous supercapacitor dynamics.

Experimental validation of GCD-CPM modeling

We now validate molecular modeling with GCD-CPM through experimental galvanostatic measurements. The supercapacitor takes the same electrolyte as modeled in our simulation. The nanoporous carbon electrode has the averaged pore size very close to that in the molecular models (experimental details are in Supplementary Part 7). In the experiment, the

GCD curve has an IR drop caused by electrode resistance (Supplementary Fig. 12)^{26, 37, 38}. Because the electrode resistance is neglected in molecular modeling, the IR drop is removed from experimental GCD curves, as described in Supplementary Part 7. Such treatment helps compare the experiment and modeling but does not change the charging and discharging of electrolyte in porous electrodes (Fig. 4a vs. Supplementary Fig. 12a).

Fig. 4 | Comparison of GCD curves obtained from experiment and modeling. **a**, The GCD curve in the experiment with a period of 20 s and its fitting by the dimensionless TLM. **b**, The GCD curve of GCD-CPM with a period of 200 ps and its fitting curve by the dimensionless TLM.

The charging dynamics of nanoporous electrodes can be illuminated by the transmission line model (TLM)^{12, 39-42}. To bridge macroscale experiments and nanoscale modeling, we derive the dimensionless form of TLM for the charging and discharging process of nanoporous supercapacitors and find that the dimensionless GCD curve, described by the dimensionless potential $\Delta\bar{\Phi}$ varying with the dimensionless time $\bar{T}$, is *only* determined by the dimensionless period α (defined as the ratio of the electric current period to the system charging time constant). Details of the dimensionless TLM can be found in Methods. As shown in Fig. 4a, the dimensionless TLM provides an excellent fitting of the experimental GCD data, with a dimensionless period of 0.42. It is then used to fit the GCD curve also with $\alpha = 0.42$, obtained by GCD-CPM modeling of nanoporous systems (Fig. 4b), which presents a good agreement as well. Since GCD curves in the experiment and modeling have the same dimensionless period, their dimensionless TLM-fitted curves are the same, even though the actual periods in the experiment and modeling are 20 s and 200 ps, respectively. With regulating the electric current period, GCD-CPM modeling is well consistent with the

experiment (Supplementary Fig. 13), bridged by the dimensionless TLM. However, the fitting reveals an apparent discrepancy between the experiment and GCD-CCM modeling (Supplementary Fig. 14). As a result, only GCD-CPM could predict the correct dynamic process of charging and discharging nanoporous electrodes.

Hysteresis in the charging-discharging process

Figure 5a shows a hysteresis of ion adsorption-desorption during the charging-discharging process of nanoporous supercapacitors, which can be evidenced by the time evolution of the in-pore electrolyte density. Specifically, in the positive porous electrode, counterions (*i.e.*, anions) are attracted into pores during charging and rejected out of pores during discharging, while a reversed trend exists for co-ions (*i.e.*, cations). The desorption of counterions during discharging does not backtrack to the adsorption during charging, and the change of co-ions in the desorption process is also different from that in the adsorption process. These findings illustrate that there is a hysteresis of ion response during the charging-discharging process. Similar hysteresis loop has been experimentally observed in porous supercapacitors probed by the electrochemical quartz crystal microbalance (note that the areal densities shown here are based on the specific surface area of the porous electrode rather than the area of quartz-crystal surface used in experiments)⁴³⁻⁴⁶.

Fig. 5 | Hysteresis in nanoporous electrode systems. **a**, Green line is the mass density of in-pore electrolyte. Red and blue lines are the number densities of in-pore cations and anions, respectively. Solid (dashed) line is the discharging (charging) process. **b**, Blue line represents the charge density coming from the in-pore electrolyte, and red line is the charge density on the electrode. Results are for the positive electrode.

The hysteresis of ion adsorption-desorption can be understood by comparing the charges from the in-pore electrolyte and on the electrode (Fig. 5b). The charge change from the in-pore electrolyte exhibits a trend (increase or decrease with time) essentially the same as that on the electrode, but the change rate in the electrolyte side is slower than that in the electrode side. It reflects that ion transport in the electrolyte, especially under nanoconfinement, is sluggish compared to the charge transport through the electrode. As shown in Fig. 5b, at the beginning of a stable cycle at the positive electrode (0 ps), the total charge on the electrode is zero, while that from the electrolyte is still negative; at the time when the charging and discharging switch (100 ps), the charge from the in-pore electrolyte, in magnitude, is less than that from the electrode. Moreover, the charge change from the in-pore electrolyte in the initial stage is slower than in the rest, since both cations and anions change at a lower rate in the initial stage of the charging and discharging process (Fig. 5a). The hysteresis in the negative electrode exhibits the same trend (Supplementary Fig. 15).

There is also a hysteresis of the ion adsorption-desorption during charging and discharging in the open electrode system (Supplementary Fig. 16), though weaker than the nanoporous electrode system. Such hysteresis originates from the fact that the electrolyte ions do not respond to the electrode polarization as timely as the electrode charges do (Supplementary Fig. 17a). This hysteresis could account for the negative potentials occurring at the initial stage of the charging and the end of the discharging at the positive electrode (Fig. 2e and Extended Data Fig. 1). The details of the hysteresis and its contribution to the negative potential can be found in Supplementary Part 8 with Supplementary Fig. 16-17. Similarly, the negative value of potentials on the positive electrode of nanoporous supercapacitors can also be understood by the hysteresis of ion adsorption-desorption resulting in the negative charge from the electrolyte at the beginning of charging or the end of discharging (Fig. 5b).

Discussion

We developed a molecular simulation method to model the galvanostatic charge-discharge of supercapacitors by regulating the applied electric current and holding electrodes at constant potential (GCD-CPM). This method was employed to delve into the charging-discharging

dynamics of the open electrode and nanoporous electrode systems, compared with traditional GCD-CCM simulations. For open electrode systems, the GCD curve and dynamic EDL structure by these two methods agree well. For nanoporous electrode systems, GCD-CCM produces unphysical phenomena, including parabolic-like potential distributions on electrodes, excessive ion diffusivity, and overmuch heat generation. In contrast, GCD-CPM well captures the charging dynamics, confirmed by experimental GCD tests with a bridge of the dimensionless transmission line model. The modeling with GCD-CPM discloses the hysteresis of ion adsorption-desorption during charging and discharging, which is found to originate from the electrolyte response lagging behind the electrode charge response to the polarization. In this work, the flexibility of the electrode is not considered in our model, which could work for electrodes with neglecting deformation during charging and discharging, while for electrodes having non-negligible expansion such as MXenes^{47, 48}, electrode flexibility needs to be taken into account.

The GCD-CPM developed here could not only model the charging and discharging process of supercapacitors with applying electric currents of any form, but also can be combined with previous CPM methods in the potentiostatic mode to investigate complex charging modes at the molecular level, thereby helping to gain deep insights into dynamics mechanisms and optimal charging modes. It may also be used for other applications involving the dynamic formation and release of double layers, such as capacitive deionization⁴⁹, battery⁵⁰, superlubricity⁵¹, and electrolyte gating⁵².

Methods

GCD-CPM for modeling galvanostatic charge-discharge

We consider a classical electrochemical system containing N immobile electrode atoms (including N_{pos} positive electrode atoms and N_{neg} negative electrode atoms) and M mobile electrolyte atoms. The constant potential method considers Gaussian charge distributions for electrode atoms and point charges for electrolyte atoms as usual^{8, 9}. The fluctuating charges on electrodes with a magnitude $\mathbf{q}$ are extra degrees of freedom to keep

electrodes equipotential. The electrostatic energy of the system U_{ele} is a function of atom positions $\mathbf{X}$ and electrode charge magnitude $\mathbf{q}$ written as^{9, 16, 53}

$$U_{ele}(\mathbf{X}, \mathbf{q}) = \frac{\mathbf{q}^T \mathbf{A} \mathbf{q}}{2} - \mathbf{q}^T \mathbf{B}(\mathbf{X}) + C(\mathbf{X}). \quad (2)$$

The first and second terms in the right-hand side of Eq. 2 represent the electrode-electrode and electrode-electrolyte interactions, respectively, and the last term describes the electrolyte-electrolyte interaction. Matrix $\mathbf{A}$ depends on the position of electrode atoms, and its size is $N \times N$; $\mathbf{B}$ is a vector of $N \times 1$; C is a scalar. Details of $\mathbf{A}$, $\mathbf{B}$, and C can be found in the literature^{9, 16, 53}. The potential on each electrode atom is $\frac{\partial U_{ele}}{\partial q_i}$ (i for the electrode atom index). To model the galvanostatic charge-discharge, the total electrode charge is constrained as $Q(t) = \sum_{i=1}^{N_{pos}} q_i$ and $\sum_{i=N_{pos}+1}^{N_{pos}+N_{neg}} q_i = -Q(t)$. In this work, $Q(t)$ is a triangular wave for GCD due to the applied square-wave current (Fig. 1d). To keep electrode equipotential at any time step and meet the constraints, we need to minimize the energy

$$U_t(\mathbf{X}, \mathbf{q}) = U_{ele} - \mathbf{q}^T \boldsymbol{\phi} + Q(t) \phi_{pos} - Q(t) \phi_{neg}. \quad (3)$$

The vector $\boldsymbol{\phi}^T = [\phi_{pos} \mathbf{I}_{pos}, \phi_{neg} \mathbf{I}_{neg}]$ is for the potentials on all electrode atoms, where ϕ_{pos} (ϕ_{neg}) is the potential on the positive (negative) electrode. $\mathbf{I}_{pos}$ ($\mathbf{I}_{neg}$) is a vector of size $1 \times N_{pos}$ ($1 \times N_{neg}$), whose elements are all one. Similar to the prior CPM simulations with step-like potentials, we solve a set of linear equations to minimize U_t at each time step, then obtain ϕ_{pos} , ϕ_{neg} , and electrode atom charges $\mathbf{q}$. Mathematically, we have

$$\mathbf{M} \mathbf{x} = \mathbf{n}. \quad (4)$$

The size of matrix $\mathbf{M} = \begin{bmatrix} \mathbf{A} & \mathbf{E} \\ \mathbf{D} & \mathbf{0} \end{bmatrix}$ is $(N+2) \times (N+2)$ where $\mathbf{D} = \begin{bmatrix} \mathbf{I}_{pos} & \mathbf{0} \\ \mathbf{0} & \mathbf{I}_{neg} \end{bmatrix}$,

$\mathbf{E} = \begin{bmatrix} -\mathbf{I}_{pos}^T & \mathbf{0} \\ \mathbf{0} & -\mathbf{I}_{neg}^T \end{bmatrix}$. Unknowns of the linear equations are $\mathbf{x}^T = [\mathbf{q}^T, \phi_{pos}, \phi_{neg}]$, and

$\mathbf{n}^T = [-\mathbf{B}^T, Q(t), -Q(t)]$. Matrices $\mathbf{A}$ and $\mathbf{B}$ are the same as the prior CPM simulations with step-like potentials^{9, 16, 53}.

Molecular dynamics simulations

For the supercapacitor with open electrodes, each electrode is modeled by three layers of graphene sheets (Fig. 1a). The simulation box has a volume of $4.254 \times 4.176 \times 48 \text{ nm}^3$, with a distance of 10 nm between the innermost layers of the positive and negative electrodes. For the supercapacitor with nanoporous electrodes, each electrode is modeled as a slit-shaped pore whose walls are made by three layers of graphene sheets (Fig. 1b). The pore size of 0.67 nm is defined as the accessible gap between the two innermost slit sheets in contact with the electrolyte, and the pore length is 8 nm. The dimensions of the simulation box are 4.1 nm, 3 nm, and 32 nm. The simulation box of all systems is sufficiently large to ensure that the central region of the electrolyte reservoir is in a bulk-like state. The Lennard-Jones model of carbon atom⁵⁴ is taken for the electrode, and a coarse-grained model (Fig. 1b), which provides accurate thermodynamic and dynamic properties, is adopted for ionic liquid [EMIM][BF₄]⁵⁵.

All simulations are performed in the NVT ensemble using a customized MD software GROMACS⁵⁶ (see ‘Code availability’ for more information), with a time step of 2 fs and a Nosé–Hoover thermostat⁵⁷ at a temperature of 400K. The heat generation during the galvanostatic charge-discharge is calculated as the energy removed from the system to maintain its temperature^{57, 58}. To avoid energy drift and attain accurate heat generation, our simulations are in double-precision⁵⁶. A cutoff length of 1.2 nm is chosen to calculate non-electrostatic interactions and electrostatic interactions in real space. The electrostatic interactions in reciprocal space are computed using the particle mesh Ewald method⁵⁹ with a fast Fourier transform grid spacing of 0.1 nm. For open electrode systems, the slab correction is adopted in electrostatic interactions⁵.

For each simulation, the system is first run for 40 ns to reach equilibrium at the potential of zero surface charge. Then a square-wave current with 30 cycles is applied on supercapacitors (Fig. 1b). We averaged the results of the last ten cycles to obtain results for a stable cycle, so that the time mentioned above refers to the time relative to the beginning of the averaged cycle. For the open electrode system, the charge density of the positive electrode

grows linearly from 0 to $9 \mu\text{C}/\text{cm}^2$ in the first half of each cycle and then decreases linearly to 0 in the second half cycle. The period of applied electric current is set as 50, 100, and 500 ps. For the nanoporous electrode system, the surface charge density on the electrode is set to change linearly between 0~ $4.96 \mu\text{C}/\text{cm}^2$, with the periods of 200, 1000, and 3000 ps. For GCD-CPM, the charge on electrode atoms is obtained using the method mentioned above; for GCD-CCM, the potential at each electrode atom is computed as the sum of the potentials from real space and reciprocal space. To ensure the accuracy of the simulation results, five independent simulations are run with different initial configurations for each system.

Transmission line model for galvanostatic charge-discharge

The transmission line model (TLM) describes the potential at time t and location along pore axis z , expressed in the equation as follows^{39, 40}

$$\frac{\partial \phi}{\partial t} = \frac{l^2}{RC} \frac{\partial^2 \phi}{\partial z^2}, \quad (5)$$

where ϕ is potential, l is pore length, and R and C are the resistance and capacitance of the pore, respectively. For the galvanostatic charge-discharge, the initial and boundary conditions are

$$\phi|_{t=0} = 0, \quad (6a)$$

$$\left. \frac{\partial \phi}{\partial z} \right|_{z=l} = 0, \quad (6b)$$

$$\left. \frac{\partial \phi}{\partial z} \right|_{z=0} = -\frac{I_0 R}{l} S\left(\frac{t}{P}\right), \quad (6c)$$

where S is a square-wave function whose period and amplitude are both one. Equation 6a indicates the pore is uncharged at $t = 0$. The boundary condition in Eq. 6b is the zero normal flux at $z = l$ (corresponds to the middle position of the open pore in our simulations), and the boundary in Eq. 6c indicates the applied square-wave current with a period P and an amplitude I_0 , as shown in Fig. 1d. We define the dimensionless potential $\bar{\Phi} = \phi/I_0 R$, dimensionless location $Z = z/l$, dimensionless time $\bar{T} = t/\tau$ ($\tau = RC$ is charging time

constant), and the dimensionless period $\alpha = P/\tau$. Hence, Eq. 5 can be written in dimensionless form as

$$\frac{\partial \bar{\Phi}}{\partial \bar{T}} = \frac{\partial^2 \bar{\Phi}}{\partial Z^2}. \quad (7)$$

The initial and boundary conditions become as

$$\bar{\Phi}|_{\bar{T}=0} = 0, \quad (8a)$$

$$\frac{\partial \bar{\Phi}}{\partial Z}\bigg|_{Z=1} = 0, \quad (8b)$$

$$\frac{\partial \bar{\Phi}}{\partial Z}\bigg|_{Z=0} = -S\left(\frac{\bar{T}}{\alpha}\right). \quad (8c)$$

Accordingly, the potential difference between the positive and negative electrodes $\Delta\bar{\Phi}(\bar{T})$ changing with time during the charging-discharging process could be obtained, which is the GCD curve and given by

$$\Delta\bar{\Phi}(\bar{T}) = \frac{2}{3} + 2\bar{T} - \sum_{n=1}^{\infty} \frac{4}{n^2\pi^2} e^{-n^2\pi^2\bar{T}} + 4 \sum_{m=1}^{\infty} (-1)^m \Phi_{step}(m, \bar{T}), \quad (9a)$$

where

$$\Phi_{step}(m, \bar{T}) = \left[\frac{1}{3} + \left(\bar{T} - \frac{m\alpha}{2} \right) \right] \theta \left(\bar{T} - \frac{m\alpha}{2} \right) - \sum_{n=1}^{\infty} \frac{2}{n^2\pi^2} e^{-\left(\bar{T} - \frac{m\alpha}{2} \right)^2 n^2 \pi^2} \theta \left(\bar{T} - \frac{m\alpha}{2} \right), \quad (9b)$$

and θ is the Heaviside step function. Therefore, the relation between $\Delta\bar{\Phi}$ and $\bar{T}$, described by Eq. 9, reveals that the dimensionless GCD curve is only determined by the dimensionless period α (*i.e.*, the ratio of the period to the charging time constant of the system).

Data availability

The modeling results of galvanostatic charge-discharge of supercapacitors using CPM and CCM approaches and electrochemical measurements are available at ...

Code availability

The code modeling galvanostatic charge-discharge process in molecular dynamics simulation using CPM and CCM approaches are available from ...

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522 **Acknowledgments**

523 Authors at HUST acknowledge the funding support from the National Natural Science
524 Foundation of China (51876072, 51836003) and the Hubei Provincial Natural Science
525 Foundation of China (2020CFA093). The work at HUST is also supported by the Program for
526 HUST Academic Frontier Youth Team.

527 **Author contributions**

528 G.F. conceived this research and designed the simulation and experiment. L.Z. performed all
529 simulations; T.Z.W. carried out the experiment; L.Z. and T.Y. derived dimensionless
530 transmission line model. L.Z. and T.Z.W. drafted the manuscript. All authors contributed to
531 the discussion of results, editing, and revising the paper.

532 **Ethics declarations**

533 Competing interests

534 The authors declare no competing interests.

535 **Additional information**

536 **Supplementary Information** is available for this paper at ...

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Extended Data Fig. 1 | GCD curves with various periods for open electrode systems.

Extended Data Fig. 2 | Distribution of charge and potential on electrodes atoms in nanoporous electrode systems. a, Spatial distribution of electrode atom charge along pore axis for GCD-CPM simulations. **b,** Spatial distribution of electrode atom potential along pore axis for GCD-CCM simulations. The data is not at one moment, but a statistic average, which each time counts the data of 5 ps around it.

Supplementary Files

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