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Understanding and Calibration of Charge Storage Mechanism in Cyclic Voltammetry Curves

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Abstract: Noticeable pseudo-capacitance behaviour out of charge storage mechanism (CSM) has attracted intensive studies because it can provide both high energy density and large output power. Although cyclic voltammetry is recognized as the feasible electrochemical technique to determine it quantitatively in the previous works, the results are inferior due to uncertainty in the definitions and application conditions. Herein, three successive treatments, including de-polarization, de-residual and de-background, as well as a non-linear fitting algorithm are employed for the first time to calibrate the different CSM contribution of three typical cathode materials, LiFePO4, LiMn2O4 and Na4Fe3(PO4)2P2O7, and achieve well-separated physical capacitance, pseudo-capacitance and diffusive contributions to the total capacity. This work can eliminate misunderstanding concepts and correct ambiguous results of the pseudo-capacitance contribution, and recognize the essence of CSM in electrode materials.

Introduction: The successful commercialization of rechargeable batteries has been making a profound impact on modern industrial society and our daily life from many aspects. As the representative, lithium-ion battery (LIB) is the most state-of-art technology widely used in portable electronics (W level) and electrical vehicles (KW level).¹ Besides LIBs, various emerging prototypes based on intercalation chemistry, for instance sodium-ion battery (SIB), are also under extensive researches and seeking for potential applications

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in grid-scale energy storage systems (MW level) due to their advantages either in cost or safety.²⁻⁹

High power density and high energy density as two guiding features of electrochemical devices are often ascribed to capacitors and batteries, respectively. Capacitive charge storage through nonfaradaic process offers many desirable properties compared with conventional batteries, including charging within seconds, long-term cycling stability and the capability to deliver up to ten times more power than batteries, but its energy density is substantially lower, by at least one order of magnitude, than batteries associated with faradaic reactions.¹⁰⁻¹² Electrode materials at nano-scale can bridge the power/energy gap between traditional double layer electric capacitors and typical rock-chair type batteries, due to a large fraction of Li⁺ intercalation-deintercalation reaction taking place at the near surface. ^{11, 13} In this process, like capacitor, the reaction is kinetically facile and diffusion is not the rate-determining step (RDS), thus we call this portion of capacity as pseudo-capacitance.13-16 The determination of pseudo-capacitance was firstly proposed by Dunn et al. in 2010 based on cyclic voltammetry (CV) measurement on ordered mesoporous a-MoO3 with iso-oriented nanocrystalline walls.10 They proposed that for a redox reaction limited by semi-infinite diffusion, the peak current *i* varies with $v^{1/2}$ (*v* is the scan rate), while for a capacitive process limited by charge-transfer process, it varies with v. In other words, the current i at a fixed potential (V) originates from the combination of two separate mechanisms: capacitive effects (k_1v) and diffusion-controlled insertion $(k_2v^{1/2})$ according to:

$$I(V) = k_1 v + k_2 v^{0.5}$$
(Eq. 1-1)
$$I(V) / v^{0.5} = k_1 v^{0.5} + k_2$$
(Eq. 1-2)

According to these equations, the accumulated pseudo-capacitance can be calculated by fitting the two constants k_1 and k_2 at every potential. Since then, this method is widely adopted by hundreds of researchers on various kinds of electrode materials for LIBs¹⁷⁻¹⁹, SIBs²⁰⁻²¹ and many other prototypes batteries. ²²⁻²⁵ However, when we directly use **Eq. 1-2** to calibrate the pseudo-capacitance, here Li₂MnO₄ is taken as an example (Figure S1), some confusing issues arise as listed below.

1) The ohmic resistance is ignored, leading to the deviation of redox peak potentials between experimental data and fitting results. This phenomenon often appears in the previous reports, ¹⁰, 20-21, 23 because **Eq. 1-2** is only applicable on the conditions with the absence of ohmic polarization.

2) The residual current is not considered when the scan direction is reversed, leading to the fitted current even beyond the experimental value during the CV scope. The reason behind is that there is a significant oxidative current when reduction process begins and vice versa. Although some researchers have noticed this error,²⁵ no efficient method was proposed to address this problem.

3) The double-layer capacitance is not specifically calculated but is included into pseudo-capacitance current, rendering the over exaggeration of pseudo-capacitance. In details, the current in CV test at a certain potential is composed of three rather than two components: physical capacitance (double-layer capacitance) current, pseudo-capacitance current (surface-confined redox reactions) and diffusive current (bulk redox reactions in electrodes).²⁶ As can be seen from Eq. 1-1, the physical capacitance is not distinguished from pseudo-capacitance.

4) The two constants k_1 and k_2 at every potential are obtained by linear fitting of **Eq. 1-2** at one potential point by another, which is in the need of repeatedly calculating several hundred even several thousand times when fitting the potential window.

Herein, three successive treatment steps on CV curves, including de-polarization, de-residual, de-background, are firstly introduced to calibrate physical capacitance, pseudo-capacitance and diffusive contribution separately. Furthermore, different from conventional works to obtain the constants k_1 and k_2 at each potential by linear fitting tediously and repeatedly, we propose for the first time a novel non-linear fitting algorithm and by one-step matrix treatment calculation with MATLAB, from which all k_1 and k_2 values could be obtained simply and efficiently.

Brief on principles of electrochemistry and mathematics

De-polarization (Potential calibration)

With the increase of scan rate in CV method, the oxidation peaks would inevitably shift positively while reduction peaks move negatively due to irreversible polarization. Equivalently speaking, there is a potential deviation from equilibrium potential caused by irreversible resistance (R), which is brought mainly by independent ohmic resistance (the detailed explanation and analysis can be found in Section 3.1). To eliminate the potential polarization, we need to find the dominating R value and then restore the potential by Equation 2:

$$V_{calibrated}^{'} = V_{original} - R * I_{original}$$
 (Eq. 2)
 $Where, V_{calibrated}^{'} = Calibrated voltage$
 $V_{original}^{'} = Original(experimental) voltage$
 $I_{original}^{'} = Original(experimental) current$

After the removal of irreversible potential shift, all the potentials would be calibrated to the electrochemical potential, which apply to the universal current-potential relationship as below,

$$i = i_0 \left\{ \frac{C_o(0,t)}{C_o^*} \exp(-\alpha fn\eta) - \frac{C_R(0,t)}{C_R^*} \exp[(1-\alpha) fn\eta)] \right\}$$
(Eq.3)
$$\eta = \text{E-E}_{eq}$$

Where C_o^* and C_R^* is the concentration of oxidative and reductive state in bulk (solid) solution, respectively; $C_o(0, t)$ and $C_R(0, t)$ is the concentration of oxidative and reductive state at the reaction interface, respectively; n = electrons transferred per formula; f = F / RT.

When $0.9 \le \frac{C_o(0,t)}{C_o^*}$ and $\frac{C_R(0,t)}{C_R^*} \le 1.1$, corresponding to a non-

diffusion-controlled condition, **Eq.3** could be simplified as the well-known Butler-Volmer Equation,

 $i = i_0 \left\{ \exp(-\alpha fn\eta) - \exp[(1-\alpha) fn\eta) \right\} \quad (Eq.4)$

De-residual calibration (First step of current calibration)

As shown in Eq. 3, there is always a residual current arising from reverse reaction, that is, a reductive current during anodic process with an oxidative current during cathodic process. This residual current that will be discussed in detail in Figure 3a would be even larger when the scan rate increases because more abundant active material is left and unable to receive or release electrons, leading to the sacrifice of capacity, as well as significant oxidative and reductive ends above zero benchmark (seeing in Figure 1a, b and c). Eq. 3 and **Eq. 4** also indicates a feasible use of an exponential curve to simulate the residual current to remove it:

$$I_1 = \exp(a_1 V_{cathodic}) + b_1 \qquad (5-1)$$

 $I_2 = \exp(a_2 V_{anodic}) + b_2 \qquad (5-2)$ Where $I_1 =$ The residual current during cathodic process.

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 I_2 = The residual current during anodic process. a_1 , b_2 , and a_2 , b_3 are four variables to determine

$$a_1, b_1$$
 and a_2, b_2 are jour variables to determine.

$$I'_{de-residual, cathodic} = I_{original, cathodic} - I_1$$
(6-1)

$$I'_{de-residual, anodic} = I_{original, anodic} - I_2$$
(6-2)

Where $I'_{de-residual, cathodic} = The cathodic current after residual calibration$

 $I_{original, cathodic} = The original cathodic current$

 $I'_{de-residual, anodic} = The anodic current after residual calibration$

 $I_{original, anodic} = The original anodic current$

De-background (Second step of current calibration)

As stated above, the current in CV test at a certain potential is composed of three rather than two components: physically capacitive current, pseudo-capacitance current and diffusive current.²⁶ However, as demonstrated in **Eq. 1**, the physical capacitance is not distinguishable from pseudo-capacitance, so that we rewrite **Eq. 1** into the three components that will be discussed in detail in Figure 4b as the double-layer current (k'_1v), pseudo-capacitance current (k'_1v)

and diffusive current ($k_2 v^{0.5}$) as follow,

$$I' = k_1 v + k_2 v^{0.5} = k_1 v + k_1 v + k_2 v^{0.5} \qquad (Eq. 7)$$

Then the following steps are to determine the capacity of doublelayer capacitance and then the second step is to calibrate the current according to,

$$I''_{de-background, cathodic} = I'_{de-residual, cathodic} + k'_{1}\nu = k''_{1c}\nu + k_{2c}\nu^{0.5} \qquad (Eq. 8 - I''_{de-background, anodic} = I'_{de-residual, anodic} - k'_{1}\nu = k''_{1a}\nu + k_{2a}\nu^{0.5} \qquad (Eq. 8 - I''_{de-background, anodic} - I''_{de-background, anodic} - k''_{1}\nu = k''_{1a}\nu + k_{2a}\nu^{0.5} \qquad (Eq. 8 - I''_{de-background, anodic} - I''_{de-backgr$$

Where $I''_{de-background, cathodic} = The cathodic current after de-background calibration$

 $I''_{de-background, anodic}$ = The anodic current after de-background calibration

 $k_{1}^{'}$, $k_{1c}^{"}$ and k_{2c} are three variables in cathodic process

 k'_{1} , k''_{1a} and k_{2a} are three variables in anodic process

The double-layer current follows the relationship as,

$$dQ_{\rm d} = i^* \,\mathrm{dt} = i^* \frac{dV'}{V} \qquad (Eq. 9)$$

Thus, the double-layer current at various scan rates changes as,

$$i = \frac{dQ_{\rm d}}{dt} = \frac{dQ_{\rm d}}{dV'/v} \qquad (Eq.10)$$

Where Q_d = The double - layer capacitance

 $i = The \ double - layer \ current$

V' = The calibrated voltage after de-polarization

 $v = The \ scan \ rate$

Since this part of capacity is highly reversible and suffer from negligible decay, **Eq. 10** implies that the double-layer currents at two different scan rates have the following relationship:

$$i_1 / v_1 = i_2 / v_2$$
 (Eq.11)

which can be used to compare and calculate the double-layer capacity at different scan rates. With the acquisition of three independent components through the above three key steps, we are also able to restore the detailed results by adding the ohmic polarization in the experimental CV curves.

Non-linear fitting

From **Eq. 8-1** and **Eq. 8-2**, a pair of k_1 and k_2 should be calculated at every potential point. When calculating N points of potential in a

certain range, we must spend a lot of time to repeatedly calculate them by N*2 times of linear fitting. Instead, we propose a new non-linear solution of batch treatment, assuming the final calibrated current (after de-residual and de-background), scan rate and the variables as three matrices of Y, X and G, respectively. Through calculating Gmathematically, we can get all variables at every potential easily, and further integrate them to obtain the final physical capacitance, pseudo-capacitance and diffusive contribution separately.

Results and Discussions

With the increase of scan rate in CV test, the oxidation peaks would inevitably shift positively while reduction peaks move negatively due to polarization, equivalently caused by a non-ignorable resistance between potential and current. The experimental potential also known as terminal potential is affected by electromotive force, diffusional, electrochemical and ohmic polarizations as follows:

$$V = \varphi_{cathode} - \varphi_{anode} - IR$$

$$= (\varphi_{e, cathode} - \eta_{cathode}) - (\varphi_{e, anode} + \eta_{anode}) - iR \qquad (Eq.12)$$

$$= E - (\eta_{cathode} + \eta_{anode}) - iR$$
Where, $V = terminal \ voltage$

$$E = electromotive \ force$$

$$i = net \ current \ of \ circuit$$

$$\varphi_{e, \ cathode} = equilibrium \ potential \ of \ cathode$$

$$\eta_{cathode} = overpotential \ of \ cathode$$

$$\eta_{anode} = overpotential \ of \ anode$$
All parameters have the same meaning as after unless pointed out

In detail, if the whole reaction rate is controlled by diffusion resulting from the sluggish ion diffusion in electrolyte or electrode, which cannot meet electrons' motions in the outer loop, the equation of potential deviation and current in this situation can be expressed as:

$$\varphi_{\text{cathode (or anode)}} = \varphi_{\text{e, cathode (or anode)}} + \frac{RT}{nF} \ln(1 - \frac{i}{i_d})$$
 (Eq. 13-1)

$$\eta_{cathode (or anode)} = \frac{RT}{nF} \ln(1 - \frac{i}{i_d})$$
(Eq. 13-2)

Where, i_d = diffusion-limited current of cathode (or anode)

 $R = 8.314 J / (mol \cdot K)$, ideal gas constant

T = temperature in Kelvins

n = the number of electrons transferred in the cell reaction

 $F = the Faraday \ constant$

All parameters have the same meaning as after unless

specifically pointed out

In second case, if the whole reaction rate is predominately determined by electrochemical process (electrons transfer process), the potential change significantly affects the activation energy of redox reaction. For anodic reaction (charge process on cathode or discharge process on anode), it gives:

$$i_a = i^0 [\exp(\frac{\beta nF}{RT}\eta_a) - \exp(-\frac{\alpha nF}{RT}\eta_a)]$$
 (Eq. 14-1)

where $i^0 = exchange$ current density

$$\beta = transfer \ coefficient$$

$$\eta_{\rm a} = \varphi_{cathode} - \varphi_{\rm e, cathode}$$

And for cathodic reaction (discharge process on cathode or charge process on anode),

$$i_{c} = i^{0} [\exp(\frac{\alpha nF}{RT}\eta_{c}) - \exp(-\frac{\beta nF}{RT}\eta_{c})] \qquad (Eq. 14-2)$$
where $\alpha = 1 - \beta$
 $\eta_{c} = \varphi_{e, cathode} - \varphi_{cathode}$

The third case is much more straightforward, as all batteries have an intrinsic ohmic resistance to charge flow, resulting in cell potential loss. The ohmic polarization is ascribed to the electrical resistance in the cell configuration, including electrolyte especially from the nonaqueous electrolyte, electrode, separator, and other components. In this case, the potential shift can be described as:

$$V = iR_{\Omega} \qquad (Eq. 15)$$

The total resistance (R_t) is the sum of the three parts:

$$R_t = R_e + R_d + R_\Omega \qquad (Eq. 16)$$

As we can see in Eq. 13, Eq. 14-1 and Eq. 14-2, the relationship between potential shift and current is nonlinear, in other words, there exists nonlinear diffusion resistance (Rd) or electrochemical resistance (Re), however, Eq.15 clearly indicates that ohmic resistance (R_{Ω}) is linear. To get a deeper insight into their effects on CV shape and to extend the application scope, we firstly select several typical electrode materials for LIBs and for emerging prototype SIBs. Here 'typical' means they should be the common candidates, undergo single-phase or two-phase electrochemical reaction, and have single or multiple redox peaks. Following these principles, we have chosen three representatives, i.e. LiFePO4 with single peak undergoing twophase process,²⁷ LiMn₂O₄ for commercial LIBs with multiple peaks (Li_xMn₂O₄, $0 \le x \le 1$)²⁸⁻²⁹, and Na₄Fe₃(PO₄)₂P₂O₇ for primary SIBs with multiple peaks³⁰ to conduct our calibration. In addition, scan rate also be regarded as a factor, thus low and high scan rates have been applied to these samples as well.



Figure 1. (a), (b), (c) original cyclic voltammetry; (d), (e), (f) linear relationship of anodic/cathodic peaks; (g), (h), (i) depolarized cyclic voltammetry of LiFePO4, LiMn₂O₄ and Na₄Fe₃(PO₄)₂P₂O₇, respectively.

Shown in **Figure 1a**, b and c, no matter for LiFePO4 (single peak, with low scan rates of 0.2-0.8 mV s⁻¹), LiMn₂O₄ (multiple peaks, with low scan rates of 0.2-1.0 mV s⁻¹) or Na₄Fe₃(PO₄)₂P₂O₇ (multiple peaks, with high scan rates of 0.5-10 mV s⁻¹), all the three original cyclic voltammetry curves are inclined, and this trend would be amplified with increasing scan rate, indicating a tremendous potential shift due to one or more kinds of the above mentioned polarizations that makes the equilibrium potential difficult to be distinguished. Fortunately, the conspicuous redox peaks could give us some clues. At the peak point, the oxidative or reductive process reaches the

maximal degree, if the reaction is limited by diffusion resistance or electrochemical resistance, the potential-current shape should be nonlinear. However, to our greatest surprise when we depict the current and potential value of peak point at different scan rates in Figure 1d, e and f, a significant linear relationship appears, suggesting the total resistance is mainly contributed by ohmic resistance. We can also get hint that a steeper slope means increased ohmic resistance, which provides a simple and feasible way to directly compare the resistance of different electrochemical systems in the absence of exhausted measurement.

To further evaluate the impact weight on peak shifts, we conduct a linear fitting between current and potential, and the fitting results of the three samples are listed in **Table 1**. It's worthwhile to mention the correlation coefficient (R) is the mostly used parameter by many researchers to evaluate the linear relationship, here it can be defined as:

$$R = \frac{\operatorname{cov}(I_p, V_p)}{\sqrt{DI_p} \cdot \sqrt{DV_p}} = \frac{E[(I_p - EI_p)(V_p - EV_p)]}{\sqrt{DI_p} \cdot \sqrt{DV_p}} \qquad (Eq.17)$$

Where the I_p and V_p represents the current and potential values at five CV peaks, respectively. However, here we prefer to recommend the use of R², also known as coefficient of determination (COD), as the statistical measure to qualify the linear regression. The reason behind is that it could give a firm evidence whether there is a strong linear reliance between current and potential at peak points because this is the core foundation of our method, for example, R=0.95 only equals to COD=0.9, but COD=0.982 (the lower limiting value in Figure 1e) equals to R=0.991.

There are some important points in Table 1 worthy to be mentioned: (i) For a certain sample, the unchanged slope values during either anodic or cathodic process suggest the ohmic resistance is a constant. (ii) For a certain sample, the two linear fitting lines are approximately parallel to each other, which is another strong evidence that the total resistance is dominated by ohmic resistance, because it is independent on neither electrons' receiving nor electrons release process. (iii) The intercept and slope values are both positive, indicating that they have the same influence on CV shapes (causing the positive shift of oxidation segment and negative shift of reduction segment). (iv) The intercept value is one magnitude lower than slope value. Further calculation on the ratio of $1-R_{\Omega}/R_t$ indicates that the intercept value (corresponding to the nonlinear R_e and R_d) accounts for less than ~7% of total resistance (R_t) and could be ignored in data calibration compared to the slope value (corresponding to the linear R_{Ω}). (v) the result provides a hint that this ratio would become smaller with a wide scan range from LiFePO4, to Na4Fe3(PO4)2P2O7. In other words, ohmic polarization is the main inducement responsible for potential shift and would become predominate over electrochemical and diffusional polarizations when scan rate increases. This change trend is easy to understand as shown in Eq.15 due to the appearance of rapidly rising current at high scan rate.

After depolarization of potential calibration found in Figure 1g, h and i, the CV shapes can be corrected according to **Eq. 2** and become symmetric to the potential axis at peak positions as well as other potential values. In short, the offset of potentials in CV shapes is mainly caused by ohmic polarization, and we can correct it effectively regardless of single or double-phase electrochemical process, the peak numbers and scan rates.



Figure 2. (a) 200 fitting lines and (b) the corresponding correlation coefficient of the $I/v^{0.5}$ - $v^{0.5}$ relation at a narrow region after only depolarization. (c) 200 fitting lines and (d) the corresponding correlation coefficient of the $I/v^{0.5}$ - $v^{0.5}$ relation at a wide region after both depolarization and de-residual.

After depolarization, we used **Eq. 1-2** to verify the feasibility of our method. The concrete operations listed in Figure S2 show a selected region equally divided into N-1 intervals with N interpolating points. Then a successive linear fitting is repeatedly conducted and correlation coefficient is employed as a parameter to check the effectiveness. As illustrated in Figure 2a and b, when the narrow region of a = 4.05, b = 4.30; c = 4.30, d = 4.05 is chosen, a satisfactory linear effect can be found at each potential, because the correlation coefficient is very close to 1.0 for oxidative process and - 1.0 for the reduced segment, which prove the validity of our depolarization calibration. However, when extended the region to a = 3.75, b = 4.30; c = 4.30, d = 3.75, as shown in Figure S3, a poor [abs | (correlation coefficient) << 1.0] even reverse result (-1.0 for oxidative while 1.0 for the reductive segment) would appear, suggesting some inferiorities in our method.

Before proceeding to the next step, two issues need to be addressed clear. The first is why here we use R rather than the above mentioned R²? The reason behind this is that the reverse correlation coefficient close to -1.0 at oxidative segment will give us false guidelines and make chaos [(-1)² \rightarrow 1.0]. The other one is why we still have a better correlation coefficient in the narrow region in terms of inferiority. The answer is that the disturbance from the inferiority is negligible in this area, and we will further explain below.

As stated above, some active materials are unable to release/accept electrons when the scan direction is reversed especially under high scan rate, in other words, strong residual current is included in the observed current curve. As a result, the anodic current starts with a negative value while cathodic curve begins at positive region, which goes against its definition and causes poor or even reverse correlation coefficient in Figure S3. Therefore, it is still crucial to calibrate the deviation of experimental currents caused by residual current, and we define this operation to eliminate the adverse influence as de-residual. To address the dilemma, the mirror lines of extended trend lines beyond the scan scope are further stimulated, which degrades to zero at ∞ in theory, however, it will soon reach I = 0 in experiment when the two ends of CV region applied. As demonstrated in Figure 3a with $\nu = 0.6$ mV/s as an illustration, according to Eq. 3 and Eq.4, we could introduce two exponential curves for each scan rate, I₁ for

cathodic and I_2 for anodic would be the residual currents to further adjust the CV shapes following the relationship described in **Eq. 6-1** and **Eq. 6-2**. We could also find that disturbance from the residual current is negligible in this area, which is the reason responsible for why there is still a great linear relationship in Figure 2b even without de-residual process.



Figure 3. (a) The principle to de-residual at v = 0.6 mV/s and (b) the depolarized CV shapes after further de-residual.

layer physical capacitive near square can be found, and the current undergoes negligible change within the whole potential window. This reminds us that in CV images we could adopt the current before significant redox reaction to approximately estimate the double layer current. Note we are not using any data in Figure S4 during the following analysis. We have considered the current resulted from physical adsorption, that is, the pure physical contribution k'_1v at each scan rate as an average value before the current changes sharply. The validity of this assumption is checked by **Eq.11**. Figure S5 shows the theoretical and experimental double-layer capacitances of LMO, and Figure 4a describes the linear relationship between them. The excellent COD validates the correctness of our method and implies the negligible contribution of adsorption current.

After the three key steps including de-polarization, de-residual and de-background calibration, the following step is to repeatedly conduct hundreds or even thousands of linear regressions between the revised potential and refreshed current. However, we propose a new method of matrix process based on non-linear fitting. Here we will give an elaborate description of principles about it and we hope this may be

Table 1. Details of the fitted intercept and slope of peak current and peak potential for various samples (A=anodic, C=cathodic).

Sample	Scan range	R^2 (COD)		Slope		Intercept		$1-R_{\Omega}/R_t$	
	mV s ⁻¹	А	С	А	С	А	С	А	С
LiFePO ₄	0.2-0.6	0.999	0.997	43.34	42.56	3.46	3.38	0.073	0.074
Li ₂ MnO ₄	0.2-1.0	0.998	0.991	58.75	69.70	4.14	3.98	0.054	0.066
Na4Fe3(PO4)2P2O7	0.5-10	0.997	0.995	97.23	106	3.29	2.83	0.034	0.026

 Table 2. Parameter values of exponential decay curves for different scan rates.

Scan rate(mV/s)	а	b	С	d
0.2	3.6867	57816.40	4.3823	84571.67
0.4	3.7020	13113.35	4.3793	20632.62
0.6	3.6948	3786.15	4.3696	5655.98
0.8	3.7049	1492.39	4.3493	2229.18
1.0	3.7211	739.58	4.3251	1133.67

The two parameters of every exponential curve are calculated with the two groups of data (the first and the last of each CV segment), and the details are exhibited in **Table 2**. When the depolarized curves are further adjusted by de-residual process, a refreshed CV shapes in Figure 3b are brought out, in which all the residual currents are eliminated. Thus, at the beginning of anodic and cathodic process, every curve starts at zero. Then we could further conduct the linear regression based on **Eq. 1-2** to verify the effectiveness of our deresidual treatment. As shown in Figure 2c and d, within the same extended region applied above, all the correlation coefficients are elevated to above 0.95, reinforcing the rationality and preciseness of the de-residual calculation.

The de-polarization treatment would eliminate the potential offset mainly caused by ohmic resistance while de-residual calibration would alleviate the experimental current from residual reaction. However, as can be seen from Eq. 1-1 and Eq. 1-2, the current corresponding to double layer capacity in CV curve is included in pseudo-capacitance current, which will lead to overestimation of pseudo-capacitance contribution. To exclude it from the total current, we have rewritten the Eq. 1-2 into Eq. 7 to determine the doublelayer current ($k'_1 \nu$), pseudo-capacitance current ($k''_1 \nu$) and diffusive current ($k'_2 \nu^{0.5}$) separately. As reasonably, double layer current $k'_1 \nu$ is a constant originated from the period before the potential reaches the equilibrium value, and remain unchanged during the whole potential window. To approve this inference, we replace LMO with active carbon and pair it with the same binder and Super P as well as the same ratio. The result is shown in Figure S4, a significant doublean alternative but simplified as well as effective method in the future. At any certain potential V_n , the pseudo-capacity and diffusive redox capacity could have originated simultaneously, we can consider the mathematical relationship between them by rewriting **Eq. 8-1** of anodic process as:

$$I_{jn} - k_{1n}' v_j = k_{1n}'' v_j + k_{2n} v_j^{1/2} \qquad (Eq.18-1)$$

$$y_{jn} = I_{nj} - k'_{1n} v_j$$
 (Eq.18-2)

$$y_{in} = k_{1n} v_i + k_{2n} v_i^{1/2}$$
 (Eq.18-3)

Where n means the nth point of potential while j represents the jth cycle scan, when j varies from 1 to 5 we have,

$$y_{1n} = k_{1n}^{*} v_1^{1/2} + k_{2n} v_1^{1/2}$$

$$y_{2n} = k_{1n}^{*} v_2 + k_{2n} v_2^{1/2}$$

$$y_{3n} = k_{1n}^{*} v_3 + k_{2n} v_3^{1/2}$$

$$y_{4n} = k_{1n}^{*} v_4 + k_{2n} v_4^{1/2}$$

$$v_{en} = k_{1n}^{*} v_5 + k_2 v_5^{1/2}$$

Rewrite it into matrix form,

$$\begin{pmatrix} y_{1n} \\ y_{2n} \\ y_{3n} \\ y_{4n} \\ y_{5n} \end{pmatrix} = \begin{pmatrix} v_1 & v_1^{1/2} \\ v_2 & v_2^{1/2} \\ v_3 & v_3^{1/2} \\ v_4 & v_4^{1/2} \\ v_5 & v_5^{1/2} \end{pmatrix} \begin{pmatrix} k_{1n} \\ k_{2n} \end{pmatrix} \qquad (Eq.20)$$

When we extend the n from 1 to N, we have,

$$\begin{pmatrix} y_{11} & y_{12} & \cdots & y_{1N} \\ y_{21} & y_{22} & \cdots & y_{2N} \\ y_{31} & y_{32} & \cdots & y_{3N} \\ y_{41} & y_{42} & \cdots & y_{4N} \\ y_{51} & y_{52} & \cdots & y_{5N} \end{pmatrix} = \begin{pmatrix} v_1 & v_1^{1/2} \\ v_2 & v_2^{1/2} \\ v_3 & v_3^{1/2} \\ v_4 & v_4^{1/2} \\ v_5 & v_5^{1/2} \end{pmatrix} \begin{pmatrix} k_{11}^* & k_{12}^* & \cdots & k_{1N}^* \\ k_{21} & k_{22} & \cdots & k_{2N} \end{pmatrix}$$
 (Eq.21)
Which can be further denoted as:

$$Y=XG$$
 (Eq.22)

Where Y, X and G are the above three matrixes successively. Then we can obtain any $k_{1n}^{"}$ and k_{2n} at each potential by solving the above matrix equation, but X is not square matrix thus there exists no inverse matrix (the pseudo-inverse matrix is not discussed here). Mathematically we can construct a square matrix by multiplying the transposed matrix X^T to its left to obtain a square matrix $X^T X$. To note, since the row number of X is far larger than its column number $(j \ge 2)$, $X^T X$ won't generate an unreliable singular matrix, thus Eq.22 has a unique solution. Consequently, G can be figured out by, $X^T Y = X^T X G$

(Eq. 23 - 1)

Where

$$\boldsymbol{X} = \begin{pmatrix} \boldsymbol{v}_1 & \boldsymbol{v}_1^{1/2} \\ \boldsymbol{v}_2 & \boldsymbol{v}_2^{1/2} \\ \boldsymbol{v}_3 & \boldsymbol{v}_3^{1/2} \\ \boldsymbol{v}_4 & \boldsymbol{v}_4^{1/2} \\ \boldsymbol{v}_5 & \boldsymbol{v}_5^{1/2} \end{pmatrix}$$

 $(X^T X)^{-1} X^T Y = G \qquad (Eq. 23 - 2)$

 X^{T} is the transposed matrix of X and $(X^{T}X)^{-1}$ is the inverse matrix of $X^T X$.



Figure 4. (a) The comparison of theoretical and experimental doublelayer capacitance of LMO. (b) The calibrated double-layer (physical), pseudo and diffusive current in the CV image after de-residual at 0.4 mV/s. (c) Details of the three components contribution at various scan rates. (d) The restored double-layer (physical), pseudo and diffusive current in the experimental CV image at 0.4 mV/s.

Following these algorithms, we can conduct nonlinear fitting, and then will obtain the value of G by solving the above matrix. Since represents the corresponding constants of the any row $(v_i - v_i^{1/2})$ at the scan rate j at the nth point, thus the capacitive and diffusive contribution at point n, scan rate j are the results of the first , respectively. The mathematical and second term of (v_i) data processing method is essentially a widely accepted least squares

method and the correctness is also proved in the Supporting Information.

Figure 4b is the calibrated double-layer (physical), pseudo and diffusive current in the CV after de-residual at 0.4 mV/s while Figure 4d is the restored details by adding the ohmic polarization in the original experimental CV image. The Figure 4b is used to determine

the contribution of the three components while Figure 4d is the restored double-layer (physical), pseudo and diffusive current in the experimental CV image when we applied polarization to them. All the corresponding contribution details after de-residual and in initial CV curves can be found in Figure S6 and Figure S7, respectively. We can find that the diffusive ratio is a little larger in oxidative part than that of in reductive part. To unveil this puzzle, we have calculated the diffusion coefficients of LMO, LFP and NFPP, and the satisfactory fitting relationships are illustrated in Figure S8, Figure S9 and Figure S10 successively. Further calculations show the apparent diffusion coefficients of LMO are 9.52*10⁻¹¹ and 7.02 *10⁻¹¹ cm²/s for oxidative peaks and reductive peaks, respectively. This result is in coincidence with Figure 4b and d that the diffusive current is getting smaller in cathodic segment. In other words, there is a slightly increased resistance for Li ions to insert into compared to extract from the crystal lattice. Please note the comparison between the two different samples like LFP and NFPP is meaningless because of the significant difference in electrochemical activity. It's also easy to find in Figure 4c that the contribution of Pseudo part is overwhelming while diffusive component is decreasing when scan rate increases, and in some report, the authors found the Pseudo contribution even above 90%,25 The reason behind this can be explained by the diffusion formula,

$$r^2 = t * D_{ion} \qquad (Eq.24)$$

Where r is the average diffusion distance, t is the diffusion time, and Dion is the diffusion coefficient. As proved by the above calculation, Dion can be roughly regarded as a constant. The three charge storage mechanisms are schematically shown in Figure 5.



Scan rate (mV s⁻¹)

Figure 5. Schematic illustration of the three charge storage means at low and high scan rate

In essence, both diffusive and Pseudo capacity are originated from Faradic reactions, which is primarily distinct from double layer capacitance where charge is stored through physical interaction at rough surface. In meantime, the only difference between the diffusive and the Pseudo portion is the length of reaction route caused by electrons-ions imbalance. Since CV undergoes potentiodynamic scan process, the diffusion time t will be smaller when scan rate v increased, therefore a smaller diffusive r or decreasing diffusive component will be expected. In contrast, because the Pseudo current is kinetically facile and diffusion is not the rate-determining step, the increased scan rate doesn't have significant influence on the Pseudo capacity. Equivalently, Li or Na ions are unable to diffuse into the deep part of a bulk material due to the limited time at high rate, leading to the capacity decay as well as the relatively increased Pseudo contribution to the total capacity in Figure 4c.

To extend the application scope of our method, by following the same calibration steps and calculating algorithm, we also specify the capacitive contribution for single-peak electrode material LiFePO4 (undergoing two-phase process) at low scan rate ranges, which has small destructiveness thus a more complete CV images are obtained. The results of calibrated double-layer (physical), pseudo and diffusive current in the CV after de-residual at various scan rates can be found in Figure S11 while Figure S12 shows the restored details in the original experimental CV image. And for Na₄Fe₃(PO₄)₂P₂O₇, a typical cathode material for sodium ion batteries, the feasibility of our method under much more complicated conditions (CV with multiple peaks and in an extended scan range) is also tested in Figure S13. The green marked areas are responding to the pseudo current and blue curves means the calibrated and restored diffusive current. After all the rational steps, a remarkable and ordered image from the three components could be obtained in Figure S6 and Figure S11, but in the CVs with the ohmic polarization in Figure S7 and Figure S12, a distorted and disordered results would appear.

Conclusion and outlook

We firstly propose a method including three key steps in terms of de-polarization, de-residual, de-background to precisely calibrate the pseudo-capacitance contribution in CV curves. In addition, we also provide an alternative non-linear fitting algorithm based on matrix manipulating to facilitate the accuracy and efficiency. Based on these fundamentals, we successively conducted matrix process on LiMn2O4 undergoing single-phase process with multiple peaks and low scan rates, LiFePO4 undergoing two-phase process with single peak and low scan rates, Na₄Fe₃(PO₄)₂P₂O₇ undergoing single-phase process with multiple peaks and high scan rates to obtain the physical capacitance, pseudo-capacitance and diffusive contribution separately. During the calibrating process, electrochemical analysis, coefficient of determination (R²), correlation coefficient (R), comparison of theoretical and experimental double-layer capacitance, fitting of diffusion coefficient and the diffusion formula are employed one by another as threshold requirements to analyze and check the calibration validity. This work will help to eliminate ambiguous concepts and understandings in the previous reports while provide a more rational and reliable method to calculate the pseudo-capacitance contribution.

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Table of contents



Well-separated physical capacitance, pseudo-capacitance and diffusive capacity are achieved from the CV curves of typical electrode materials for metal-ions batteries after three successive treatments including de-polarization, de-residual and debackground as well as non-linear fitting calculation, offering a more rational and reliable method to calculate the pseudocapacitance contribution.