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1 **Electron delocalization and electrochemical potential distribution phenomena in**
2 **Faradaic Electrode Materials for understanding electrochemical behavior**

3
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16

17 **Abstract**

18 Electrochemical energy storage devices are built upon the foundations of batteries and
19 supercapacitors. In the past decade, new types of electrode materials, such as pseudocapacitor-
20 like species, have been intensively developed to obtain superior performance in terms of energy
21 density and power. Pseudocapacitive materials store charge through Faradaic redox processes,
22 while their electrochemical signature remains mystically similar to that of electrochemical
23 double-layer capacitors, even though it is caused by redox processes. To address this
24 controversy, we introduce an all-inclusive analytical model for evaluating the voltammograms
25 of electrode materials. In view of this, the present article focuses on understanding the origin
26 of the pseudocapacitive phenomena in the electrochemical signal (such as cyclic voltammetry,
27 CV). Based on the self-exchange electron transfer mechanism and tunneling effect within the
28 atomic structure of solid electrode materials, pseudocapacitive materials possess a high degree
29 of electron delocalization possibility related to the number of redox centers. This process
30 initiates the electrochemical potential distribution among the neighboring redox sites, which is
31 consequently observed in electrochemical signal as the plateau feature in CV like in EDLC.
32 We proposed for the first time the determination of capacitive tendency of various faradaic
33 electrode materials, which turned out to be relative to the number of redox center (n) and total
34 charge (z) as presented in this work as a functional type of electrode material classification
35 plot. Here, we proposed the theoretical link of electron hopping, likely occurring when the
36 number of redox centers are large. The developed all-inclusive model is versatile to predict
37 rate/potential regimes for the maximum faradaic storage, and then well differentiates the
38 pseudocapacitor- materials from battery- materials.

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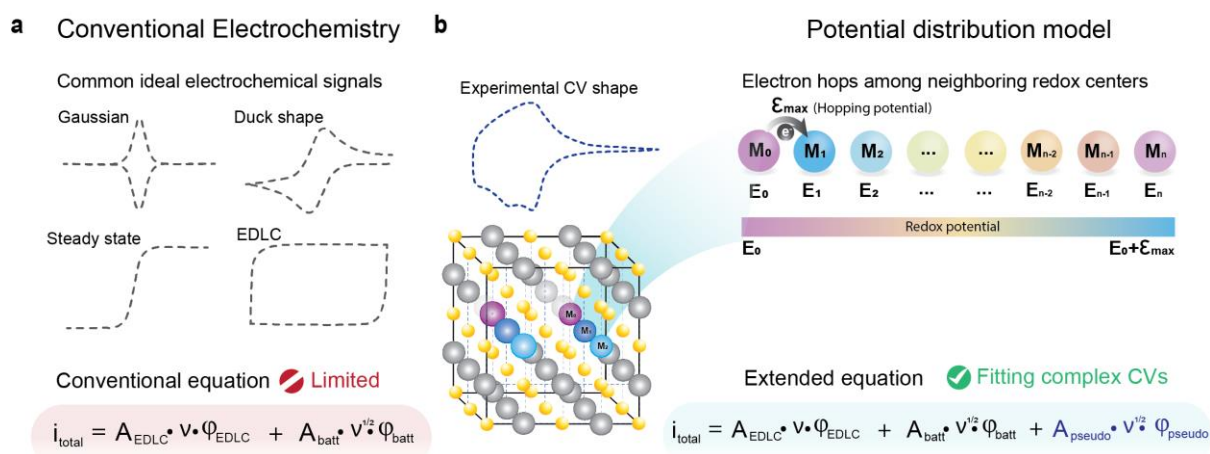
42

43 **Introduction**

44 The ever-growing global demand for energy underwent a sharp and sudden increase, leading
45 to the expansion of energy storage technologies. Many of these storage technologies, most
46 notably electrochemical energy storage, rely on redox processes¹. The chemical composition
47 of electrodes has been the topic of many studies to improve the performance of electrode
48 materials in terms of energy and power densities^{2,3}. Within this multiplicity of compositions,
49 nanostructures and properties, electrode materials are classified into two categories: non-
50 Faradaic and Faradaic electrode materials. A non-Faradaic reaction points to one in which there
51 is an absence of electron exchange across the electrode-electrolyte interface. In this case,
52 charge storage occurs as a consequence of charging the electrochemical double layer at the
53 electrode-solution interface. When Faradaic processes are engaged, however, electrons are
54 transferred across the current collector to or from redox centers contained inside the electrode.
55 Redox centers are buried in a solid phase, and the charging process thus involves the motion
56 of counterions. The difference between these electrode materials is electrochemically
57 detectable and is analyzed according to their physicochemical traits. Numerous characteristics
58 are determined using a variety of methods, including electrochemical impedance spectroscopy
59 and cyclic voltammetry (CV)^{4,5}. The CV technique has the advantage of varying the cell
60 voltage (or potential, in a 3-electrode system) and observing the impact of these fluctuations
61 on the cell dynamics (i.e., electron and ion transfer), while modulating the scan rate, *i.e.*, the
62 time scale of the material studied.⁶ While non-Faradaic electrode materials produce a box-
63 shaped signal during CV measurements, Faradaic electrode materials present current peaks,
64 indicating the potential value of their redox center.⁷ However, Faradaic electrode materials are
65 only seldom amenable to analysis through a perfect Gaussian peak signal, as idealized by the
66 notion of immobilized redox centers (**Fig. S2a**). Similarly, a thorough examination of the

67 $i=f(E)$ curves reveals that Gaussian peaks are not perfectly symmetrical (see **Fig. S2b** for the
68 ideal electrochemical response).

69 Surprisingly, there are no contemporary theories or formalist frameworks that make clear
70 the story of faradaic materials well. To compound the issue, many more questions arise when
71 addressing pseudocapacitive materials, which are characterized as Faradaic electrode materials
72 that exhibit a box-shaped signature during a current-potential measurement (CV) ⁸. Two
73 unsolved questions today are: firstly, how might it be possible to sign a Faradic phenomenon
74 with a curve comparable to that of an electric double-layer capacitor (EDLC) material when
75 the established signature must be Gaussian; secondly, which similarities and differences are
76 present when comparing a Gaussian ideal material to a material with pseudocapacitive
77 properties? The pseudocapacitor's box-shaped CV has been observed in a wide variety of
78 transition metal oxides ⁹, conducting polymers ¹⁰, and other semiconducting redox materials.
79 The mechanisms by which Faradaic reactions may exhibit quasi-rectangular capacitive
80 electrochemical behavior remain unknown, and no cohesive model explaining the peculiarities
81 of Faradaic electrode materials exists in the literature. Numerous studies, however, serve to
82 demonstrate this pseudocapacitive behavior (**Fig. S1**) ^{2, 4, 11-44}. This thus leads one to consider
83 the possible reasons for a redox reaction, which is essentially a Faradaic occurrence, deviating
84 so far from the ideal peak response (as illustrated in **Figure 1**).



85

86 **Fig. 1** | (a) Conventional electrochemistry signals in ideal CVs with the conventional equation
 87 are limited to describe only simple CVs. (b) Potential distribution model within the electrode
 88 material structure based on electron transfer between redox centers (M_0, M_1, \dots, M_n) with the
 89 redox potentials respectively to each redox site. And our new extended equation for the total
 90 current leads to the first-time complex CV fitting.

91

92 **Fig. S3a** illustrates the many and varied Faradaic electrode materials (*i.e.*, those
 93 concerned with electron transfer), including both those used in pseudocapacitors as well as
 94 those used in batteries. Regardless of which technical device is concerned, the electrode
 95 component, including its active material, stays constant. The active material stores charges
 96 through redox reactions involving the crystalline structure's redox center (as illustrated in
 97 **Figure 1**). As a result, this active material may be regarded as a matrix, with redox centers
 98 being connected by covalent bridges (**Fig. S3b**, *e.g.*, oxygens) that lead these redox centers to
 99 interact. Naturally, the true nature of materials remains multifaceted, including hierarchical
 100 porosity, multicrystalline structures, the presence of binders, conductive additives, and the
 101 percolation of highly conductive carbons near oxide particles.

102 In order to comprehend and rationalize the wide range of electrochemical reactions
103 observed in Faradaic electrode materials (including pseudocapacitive materials), a three-step
104 strategy is provided herein. The first step involves categorizing the relevant materials according
105 to their n (number of redox centers per nm^3) and Z (electron included in crystalline structure)
106 values. These parameters bring the effect of the n and Z values on the electrochemical signature
107 to light. In the second step, the influence of n and Z is then rationalized using a certain
108 microscopic approach centered on electron transfer (*i.e.*, the transition-state model). The third
109 and final step, enabled by the first two in terms of creating a collection of parameters, makes
110 use of these to simulate and compare theoretical and experimental electrochemical signal
111 responses.

112

113 **Results and discussion**

114 As stated before, there is no available model that combines the behavior of a battery with that
115 of a pseudocapacitor currently. To complicate matters, these concepts are often separated into
116 two distinct categories. This means that researchers find themselves without a coherent,
117 universal method for analyzing and decoding electrochemical behavior (*i.e.*, the shape of the
118 cyclic voltammogram). A unified technique could be considered a significant step towards the
119 future development of innovative, high-power batteries. We thus propose an integrated model,
120 demonstrating that pseudocapacitive contributions indeed also exist in battery materials (Li-
121 ion, Na-ion, Mg-ion). CVs of batteries demonstrating their cell dynamics (electron and ion
122 transport) are also shown to deviate significantly from the ideal signals published in the 1980s.

123 **The number of redox centers per nm³ and the Z value as simple markers for** 124 **distinguishing between pseudocapacitive and battery materials**

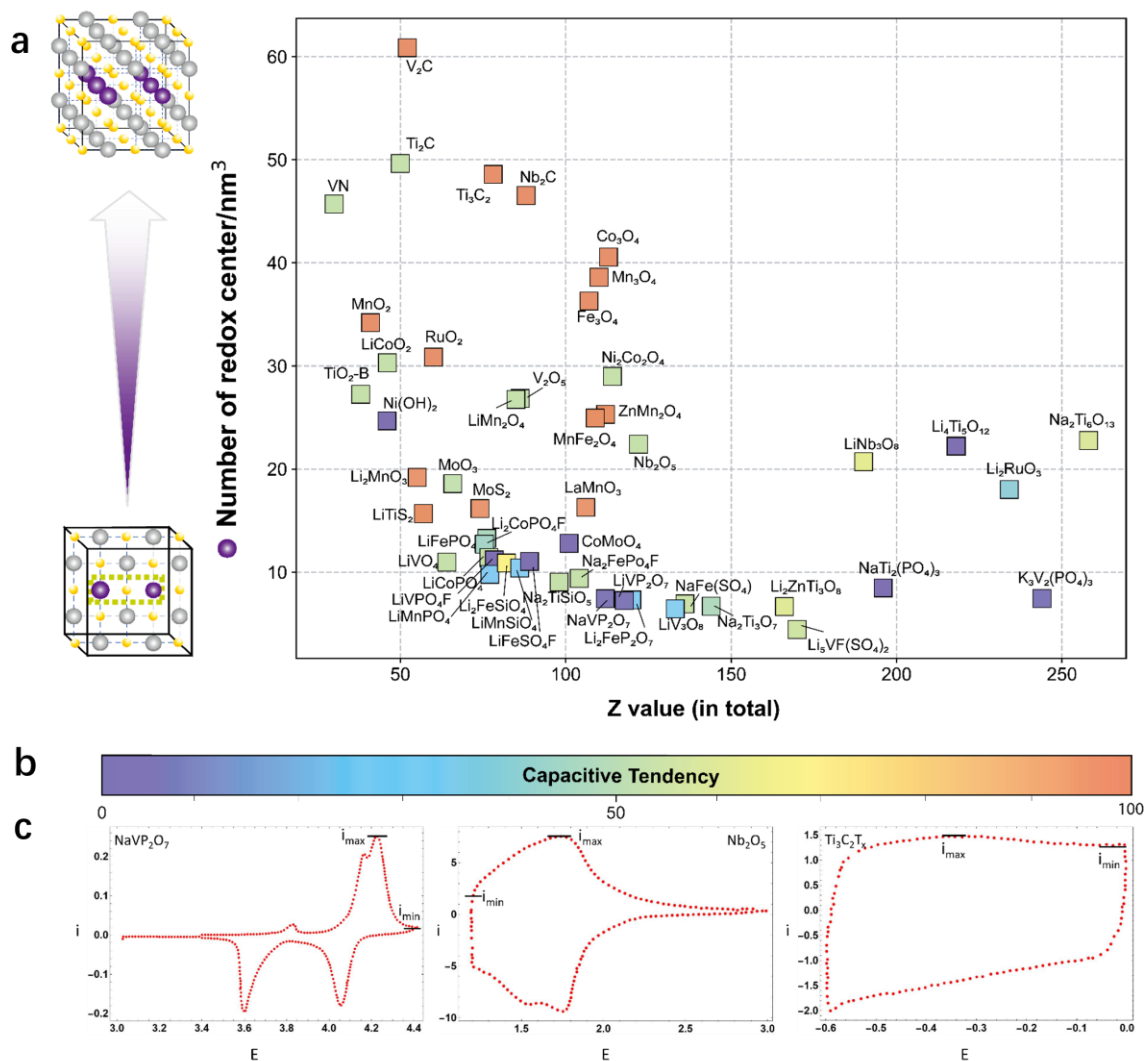
125 The primary goal is to be able to compare Faradaic electrode materials using three simple
126 markers: (i) n , the number of redox centers per nm³ calculated as described in the Supporting
127 Information (Section 5), (ii) Z , the number of electrons included in the crystalline structure,
128 and (iii) *capacitive tendency*, the ratio of peak current to plateau current is named
129 pseudocapacitive percentage. The number of redox centers per cubic nanometer and the
130 number of electrons per crystalline structure were determined for a series of lithium-ion
131 batteries and pseudocapacitive materials. We compiled a list of fifty materials that are the most
132 often used in electrochemical energy storage devices. Furthermore, we established a new
133 parameter, *the capacitive tendency*. Capacitive tendency is the parameter to describe the
134 electrochemical behavior of materials. This predictive model was published by some of us.¹¹⁵,
135 using deep learning to classify electrochemical signals. The specific research involves using
136 image classification to distinguish different curve shapes (rectangular shape and peak shape)
137 that act on electrochemical signals, such as cyclic voltammetry, to connect electrochemical
138 information (pseudocapacitor and batterie). When the capacitive tendency is close to 100%,
139 the curve is more rectangular, and the material is more like a supercapacitor. When the
140 capacitive tendency is close to 0%, the curve is more like a peak shape and the material is more
141 like a battery. The capacitive tendency analyzes the shape of the voltammogram.

142 The capacitive tendency and capacitive contribution are not the same concept. *Bruce Dunn*
143 *et al.*¹¹⁶ proposed a model in 2007 that is proportional to current and scan rate, and used this
144 model to describe the capacitive contribution and diffusion contribution in materials. The
145 capacitive contribution is different from capacitive tendency proposed by some of us, because
146 the capacitive tendency is a metric to describe the shape of the material's signal curve and
147 classify the material, rather than to calculate the proportion of capacitive contribution inside
148 the material or provide the percentage of EDLC, pseudocapacitor or battery.

149 Alternatively, there is another simple way to calculate and express rectangular shape,
150 which is called capacitive percentage, or simply *%capa* (see ESI section 5 and Fig. S5).
151 Equation 1 defines this pseudocapacitive percentage, but this result is just an approximate
152 result. This one can only explain the general trend, and capacitive tendency is the result more
153 accurate.

$$154 \quad \%_{capa} = 100 - \frac{i_{max} - i_{min}}{i_{max}} \cdot 100 \quad \text{Eq. 1}$$

155 Where i_{max} is the maximum current and i_{min} is the relative minimum current taken after the
156 faradaic contribution. **Figure 2** shows a heatmap of capacitive tendency of all materials
157 researched in the work.



158

159 **Figure 2. State-of-the-Art in Faradaic electrode materials for batteries and**
 160 **pseudocapacitors.** (a) represents a list of materials classified according to capacitive tendency
 161 (ascribed to the color bar). The Y-axis represents the number of redox centers per nm³ and the
 162 X-axis represents the total number of electrons in the crystal structure. (b) the qualitative color
 163 bar representing capacitive tendency. (c) represent typical voltammograms of the
 164 corresponding electrode material.

165 This computation makes it possible to account for the nuances inherent in the
 166 voltammogram shapes as measured in the CV experiments. The %*capa* is a useful indicator
 167 when it comes to anticipating the degree of charge delocalization. On the one hand, if the local
 168 minimum current is close to the maximum current, then the current is identical and the behavior

169 displayed is rectangular (noting that the global resistance of the device is not taken into account
170 in the calculation). This rectangular voltammogram represents the signature of so-called
171 supercapacitive substances, be they EDLCs or pseudocapacitors. On the other hand, if the
172 difference is significant, *i.e.*, the redox peak is highly prominent, then the behavior displayed
173 is battery-like. Indeed, in order to accurately depict the electrochemical behavior of the real-
174 world voltammograms, calculating the %*pseudo* thus allows for a simple categorization of the
175 voltammogram shape, regardless of the material composition or lack thereof. The *capacitive*
176 *tendency* is a graphical descriptor of a curve $i=f(E)$ that is independent of the usual material
177 classification (battery, EDLC, pseudocapacitor).

178 The result of combining the redox center number per nm^3 with the electron number Z of
179 the crystalline structure is shown in Fig. 2. The cell count is based on the volume of each cell
180 (see the CIF file, in ESI), and the cell unit's Z' value indicates the number of material crystalline
181 units repeated in one cell volume. In addition, capacitive tendency is used for over forty
182 materials involved in the manuscript and compared it with the %*pseudo* results calculated from
183 Equation 1, the complete result table is Table S4 in ESI.

184 In **Fig. 2, S7-S8**, a scatter plot with a gradient of different colors denoting the *capacitive*
185 *tendency* is used to position the 50 different materials ^{5, 45-91}. Each of these materials is
186 accompanied by voltammograms which were extracted from scientific publications. They were
187 selected due to the fact that they are the most frequently applied materials in batteries and
188 pseudocapacitors. For decades, these materials have been in constant evolution with the
189 synthesis of new materials, the design of new structures, adjustments to their inner nature, and
190 modifications to their morphology, all of which were geared towards maximizing the
191 capacitance/capacity to build advanced energy storage devices. As far as pseudocapacitive
192 materials are concerned, RuO_2 stands out as one that underwent years of trials before finally
193 shedding light on the mechanism of redox reactions in aqueous acidic electrolytes. This had to

194 do with the valence change from Ru^{4+} to $\text{Ru}^{3+}/\text{Ru}^{2+}$, associated with proton insertion ⁹²⁻⁹³.
195 Another prominent one is MnO_2 , which possesses a smooth ionic diffusion but displays limited
196 electronic conductivity ⁹. These two laid the groundwork for further research involving metal
197 oxide-based Faradaic electrode materials, such as TiO_2 , Nb_2O_5 , Co_3O_4 , Mn_3O_4 , Fe_3O_4 , etc. In
198 the case of Co_3O_4 , it was found that morphological changes and size could lead to distinctive
199 electrochemical behavior, since when nanosized it triggers a high-rate redox reaction.¹⁰⁵ Aside
200 from metal oxides, carbides and nitrides (*e.g.*, vanadium nitride) also become the subject of
201 research relating to redox reactions in pseudocapacitive materials. Among them, 2D MXenes,
202 such as Ti_3C_2 , Ti_2C , V_2C , prevail due to their intriguing electronic conductivity and high-rate
203 capability ^{106, 107}. Numerous battery materials have been studied for use as anodes and cathodes
204 in various battery cells. Current cathode materials that have already been commercialized
205 include the well-known LiCoO_2 and LiFePO_4 ^(ref 94). On the anode side, the most notable are
206 LiTi_4O_5 and TiO_2 ^(ref 95). It has been ascertained that battery materials exert redox reactions
207 following phase changes after intercalating ¹⁰⁸⁻¹¹¹. The materials selected for this study all serve
208 to contribute to an overall picture of Faradaic electrode materials.

209 We observe an unmistakable trend whereby pseudocapacitive materials display a redox
210 center density of between 20 and 60 per nm^3 and a Z value of between 0 and 120. In other
211 words, a pseudocapacitive material has a large number of redox centers with a low number of
212 electrons inside its crystalline structure. For battery materials, the number of redox centers are
213 never greater than 30 per nm^3 , while Z values can reach up to 140.

214 More specifically, MnO_2 and RuO_2 both show a *capacitive tendency* of close to 100%
215 with a large number of redox centers per nm^3 and low Z values. Mn-based materials can be
216 battery-type ones such as Li_2MnO_3 ^(ref 85), $\text{Li}_2\text{MnSiO}_4$ ^(ref 91) and LiMnPO_4 ^(ref 59) or
217 pseudocapacitor-type ones such as MnO_2 ^(ref 13). The same goes for Ti, with battery-type ones
218 such as LiTiS_2 ^(ref 80), $\text{Na}_2\text{TiSiO}_5$ ^(ref 54), $\text{NaTi}_2(\text{PO}_4)_3$ ^(ref 78), $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ^(ref 66) and $\text{Na}_2\text{Ti}_6\text{O}_{13}$ ^(ref 81),

219 and pseudocapacitor-type ones such as Ti_2C ^(ref 29) and Ti_3C_2 ^(ref 11). Some materials are not a
220 good fit for this simple classification, such as MoS_2 ^(ref 51) and MoO_3 that show around 17 redox
221 centers per nm^3 and a Z value of around 70, all the while displaying pseudocapacitive behavior.
222 Co_3O_4 , Mn_3O_4 and Fe_3O_4 exhibit large densities of redox centers together with high Z values,
223 with *capacitive tendency* values of around 50%. 2D MXene materials, including Ti_3C_2 and
224 V_2C , are pseudocapacitive materials with high redox center densities and low Z values. It
225 should be noted that the choice of electrolyte probably has an impact on the *capacitive tendency*
226 value. For example, for $\text{Ti}_3\text{C}_2\text{T}_x$ -MXene ^(ref 29), the *capacitive tendency* value decreases from
227 80 to 50% (in KOH and H_2SO_4 , respectively). V_2C -MXene ^(ref 72) shows similar results.
228 Concerning MnO_2 in an aqueous medium, the electrochemical reversibility can be highly
229 impacted depending on the pH. This can be explained by a confinement phenomenon, where a
230 transition occurs from double-layer to Faradaic charge storage.¹¹⁴ The electrochemical
231 interface actually involves porous or layered cases instead of an ideal planar model. With
232 increasing interface complexity, charge transfer improves between an electrolyte ion and the
233 host regarding the extent of ion desolvation and confinement. When K^+ intercalates in
234 birnessite metal oxide, the K^+ is still hydrated without desolvation between interlayers, which
235 offers a weak ion-host interaction and reduced charge transfer.

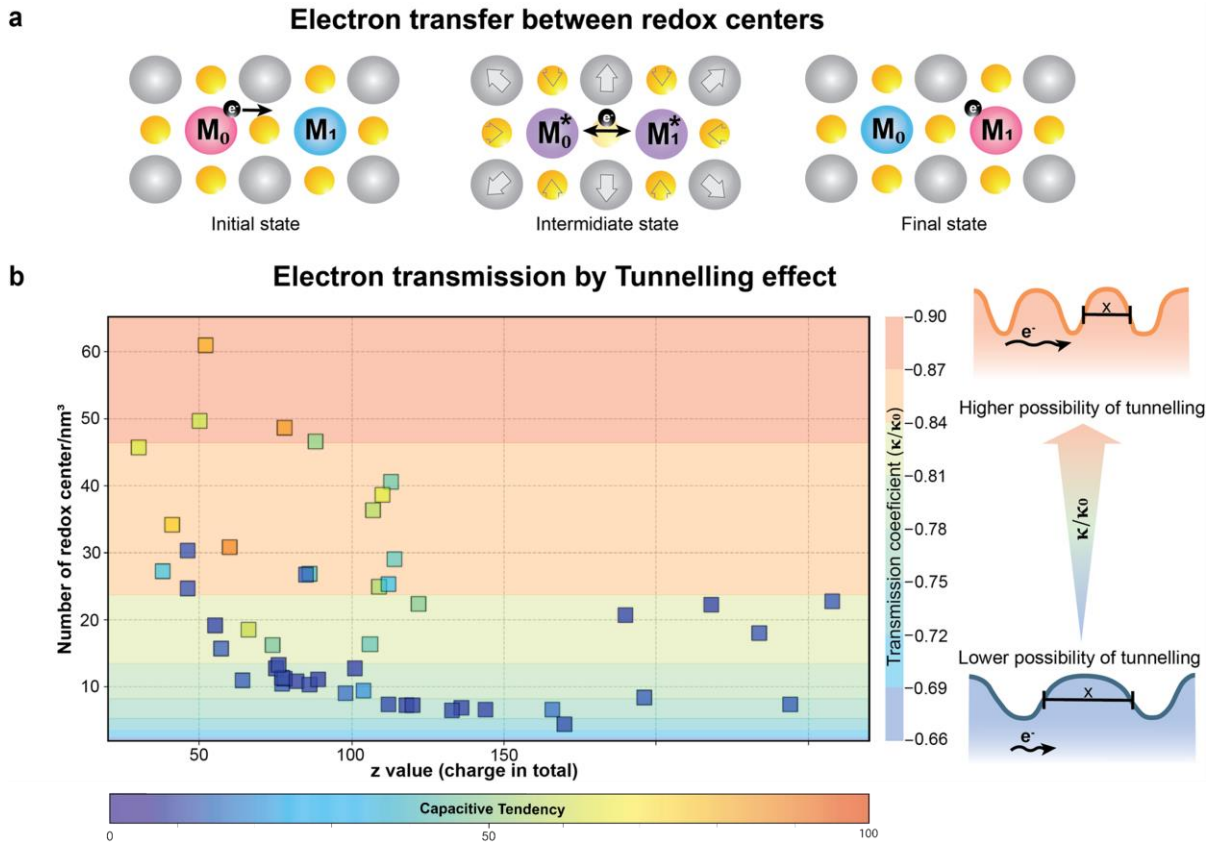
236 We have demonstrated that identifying the density of redox centers, n , and the
237 corresponding Z values is enough to accurately predict the material type and the global shape
238 of the cyclic voltammogram and vice versa. For the greater part of the researchers working in
239 the field of electrochemical energy storage materials, determining the n and Z parameters will
240 thus be quite straightforward. However, it is worth noting that the type of salt and nature of the
241 solvent used in the electrolyte may sometimes affect the electrochemical behavior, and
242 therefore the shape of the voltammogram.

243 To summarize, the *capacitive tendency*, and consequently the shape of the voltammogram,
244 is chiefly governed by: (1) the number of redox centers per nm^3 , and (2) the Z value of the
245 crystalline structure, bearing in mind that (3) the nature of the electrolyte may have a certain
246 effect on the result. It is then necessary to correlate these pieces of information within a model
247 that explains why these three parameters affect the voltammogram signal. To this end, it is
248 necessary to understand the impact that the proximity of the density of redox centers, n , has on
249 the electron moving through the Faradaic electrode material.

250 **Electron movement as a cause of redox potential distribution**

251 The initial Faradaic oxidative reactions that generate charges in the material are likely
252 connected to ionic mobility, independently of the pseudocapacitive or battery-like behavior of
253 the considered material. Therefore, the fundamental process of electron injection into a redox
254 center remains a redox reaction, which is a Faradaic phenomenon. However, the spatial
255 organization and density of the redox centers in battery and pseudocapacitive materials can
256 produce quite a different outcome. The density of redox centers has a direct impact on the
257 probability of an electron jumping from one redox center to another. Pseudocapacitive
258 materials exhibit a large number of redox centers per nm^3 , with a total exceeding 30. Following
259 a charge injection (or extraction), the charge distribution then creates a distribution of redox
260 potentials (as demonstrated in the following section). To explore this effect, we will first
261 demonstrate that the probability of transferring an electron between two redox centers is greater
262 when n is large and Z is small. In a subsequent step, we will show that an electron exchanged
263 between two redox centers has an effect on the potential of neighboring centers.

264



265

266 **Figure 3. Electron transfer between 2 redox centers.** (a) represent the atomic changes
 267 associated with electron transfer for a solid structure. (b) represents the electron transfer
 268 probability as a function of the number of redox centers (Y-axis). The background color is
 269 respected to the transmission coefficient of electron transfer according to tunnelling effect.

270

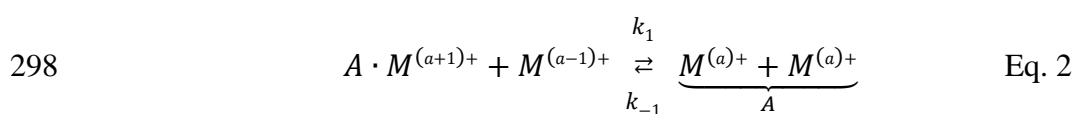
271 To understand the possibility of an electron exchange between two redox centers, the
 272 probability of an electron hopping from one redox center to another may be expressed as the
 273 product of three separate probabilities. The first probability is equivalent to the chances of the
 274 electron encountering a neighboring redox center (noting that a defect in the crystalline
 275 structure will reduce this probability). The second probability is that a phonon (the vibration of
 276 a crystal lattice) causes the local distortion necessary for the temporary equalization of donor

277 and acceptor levels (**Fig 3a**). The third probability is that tunneling occurs (**Fig.3b**), which is
278 exponentially dependent upon the distance between the two considered redox centers.

279 According to this formalism, the greater the density of redox centers, the greater the
280 probability of the electron being delocalized. This is consistent with the fact that a
281 pseudocapacitive material has a large number of redox centers per nm³, so the probability of
282 charge delocalization is non-zero. It is worth noting that in the preliminary reports about the
283 redox behavior of RuO₂, Trasatti *et al.*⁽⁹⁶⁾ emphasized this fact from the very start, stating, with
284 respect to the metal cores, that the "*Me-Me* distance and the radius of the cation in these oxides
285 are such that overlap of the inner d orbitals is possible, and the d electrons in the d bands are
286 responsible for the metallic conduction", referring to Marcus studies on electron transfer to
287 substantiate this remark⁽⁹⁷⁾.

288 One particular "chemical" description of the proximity of the redox center may be
289 investigated as a reaction comprising electron hopping. There are two alternatives when an
290 electron is injected into a redox center: (1) The injected electron is restricted to the vicinity of
291 the redox center (*i.e.*, it is localized), or (2) the electron jumps to the nearest neighbor. After
292 that, the charge is partially delocalized. This viewpoint is comparable to that of adiabatic vs.
293 diabatic electron transfer⁽⁹⁸⁾.

294 Now, the electron transfers or hops from one redox center to the neighboring one in the
295 electrode material structure. The redox reaction can be transcribed, along with the associated
296 ionic transfer (where *A* is the anion) with equilibrium constant with the equilibrium ($K_{hopping}$)
297 as follows:



299 where *a* is the reaction activity of a certain state.

300 If $k_1 \gg k_{-1}$ ($K_{hopping} \gg 1$) then the probability of an electron exchange between 2 redox
 301 centers is high. And inversely, if $k_1 \ll k_{-1}$ ($K_{hopping} \ll 1$), then the probability of an electron
 302 exchange is low. According to this equation, the way in which the redox charge is shared is
 303 based on an equilibrium constant, $K_{hopping}$. This equilibrium constant can then be expressed as
 304 the difference in redox potential required in order to oxidize both redox sites. E_0 is the potential
 305 to oxidize the first one, the so-called standard redox center, and E_1 is the redox potential of the
 306 closest neighbor.

307 E_n corresponds to the redox potential of the umpteenth neighbor, then the umpteenth neighbour,
 308 $K_{hopping,n}$ is:

$$309 \quad K_{hopping,n} = \exp \left[\frac{F \cdot (E_n - E_0)}{R \cdot T} \right] \quad \text{Eq. 3.}$$

310 Where F is the Faraday constant ($96485 \text{ in } C \cdot \text{mol}^{-1}$), R is the gas constant ($8.3145 \text{ J} \cdot$
 311 $\text{mol}^{-1} \cdot \text{K}^{-1}$), and T is temperature (293.15 K).

312 The equation **Eq. 3** highlights two critical points: (i) Firstly, when two redox centers easily
 313 exchange electrons ($K_{hopping,1} \gg 1$), then the difference in potential between the two redox
 314 centers is quite large ($E_n - E_0 \gg 0$). In other words, injecting a charge into one of the redox
 315 centers has an effect on the amount of work required to inject a charge into the redox center
 316 closest to it. (ii) Secondly, the further away a neighbor is from the standard redox center, the
 317 less likely it is for them to share an electron. The potential distributes from the first redox center
 318 (M_0) to the nearest (M_1) and other neighboring redox centers (M_n) with hopping potential (ϵ).

319 n is the total number of potential hopping in the system, which corresponds to the number of
 320 neighbors nearest to the area where tunneling is likely to occur. ϵ_{max} and ϵ_{min} are the
 321 maximum and minimum potential difference between two redox centers as demonstrated in
 322 Figure 4.

323 The neighboring redox centers (M_i , when $i = 1, 2, 3, \dots, n$ and i is the neighbor according to
 324 its position with respect to the standard redox center), the potential distributed is in descending
 325 order:

$$326 \quad E_1 > E_2 \gg E_n > E_{n+1} \approx E_0$$

327 Then, $K_{hopping,1} > K_{hopping,2} > K_{hopping,3} \gg K_{hopping,n}$

328 Firstly, among n number of redox center, started from M_0 .

$$329 \quad M_0, M_1, \dots, M_{n-4}, M_{n-3}, M_{n-2}, M_{n-1}, M_n$$

330 At the farthest redox center (M_n), the lowest energy needed for the electron to jump, ε_{min} . By
 331 recurrence sequence, the hopping potential from the farthest to the nearest neighboring redox
 332 site is in ascending order:

$$333 \quad n\varepsilon_{min}, \dots, 5\varepsilon_{min}, 4\varepsilon_{min}, 3\varepsilon_{min}, 2\varepsilon_{min}, \varepsilon_{min} \quad .$$

334 So, $E_{n-i} = E_0 + (i + 1)\varepsilon_{min}$ Eq. 4

335 When $i = 1, 2, 3, \dots, n$.

336 In this model of the redox potential distribution, there are three notable variables: ε_{max} ,
 337 ε_{min} and n . So, ε_{max} is the work difference between the two nearest redox centers ($E_1 - E_0$).
 338 When a charge is injected into the standard redox center, its nearest neighbour has the most
 339 impacted electron affinity, so its redox potential is increased by a maximum jump (ε_{max}).
 340 Whereas the minimum potential jump corresponds to the furthest redox center influenced by
 341 the charge, noted by ε_{min} . Then n represents the number of neighbors influenced by the charge
 342 injection. Note that **Eq. 3** and **Eq. 4** then become, for the general form:

$$343 \quad K_{ET,i} = \exp\left[\frac{F \cdot \varepsilon_{max}}{i \cdot R \cdot T}\right] \quad \text{Eq. 5,}$$

344 and, for the nearest neighbor ($i = 1$):

345
$$K_{ET,1} = \exp \left[\frac{F \cdot \varepsilon_{max}}{R \cdot T} \right] \quad \text{Eq. 6,}$$

346 and, for the most distant neighbor ($i = n$):

347
$$K_{ET,n} = \exp \left[\frac{F \cdot \varepsilon_{min}}{R \cdot T} \right] \quad \text{Eq. 7.}$$

348 **Fig. S3** illustrates the matrix model, including the redox potential distribution, using **Eq.**
349 **4**. When redox centers are tightly packed together, the electron affinity decreases (*i.e.*, it is
350 more difficult to inject the electron into the nearest neighbor). This model involves a large
351 redox potential distribution within the material.

352 A Faradaic electrode material is thus represented by the matrix, for which the continuous
353 phase represents the overall charge in the crystalline structure and where the color of the redox
354 centers is the distribution of redox potentials. Therefore, the proximity of the redox centers –
355 high-density n - results in a broad redox potential distribution, as illustrated by the matrix
356 model.

357 The rate constant, k_I , which is the kinetic constant of the electron transfer, is expressed by
358 considering two rate-limiting steps. The first step is to consider that the electron transfer is
359 sequential to the ion transfer. Therefore, k_I will either be the electron transfer or the transfer of
360 the counter-ion to be split. However, an alternative to this could be that the electron transfer is
361 concomitant with the ion transfer, so that the rate constant k_I will reflect a new mathematical
362 expression. Recently, Bazant *et al.* incorporated ion transfer effects into the kinetic theory of
363 electron transfer⁹⁹. The nature of the counterion can be varied: Such as Li^+ , Na^+ , Mg^{2+} , Zn^{2+}
364 etc.

365 Three phenomena influence the charge storage process in electrochemical energy storage
366 materials: (1) the tunneling effect, (2) the chemical environment of the redox center, and (3)
367 the effect of the counterion from the electrolyte. By analogy with the electron transfer in
368 solution, therefore, a link on charge processes exist. The crystalline structure, the counterions
369 and the distance between the redox centers all influence the ease with which charges can be

370 delocalized. The effect of the counterion also deserves careful consideration, since the
 371 kinetics of electron exchange will be influenced by its probability of being shared or not,
 372 resulting in charge delocalization. Significantly, the charge delocalization induced by these
 373 three phenomena results in a redox potential distribution within the Faradaic electrode
 374 materials. This framework thus allows one to pinpoint the fundamental differences between a
 375 wide range of Faradaic electrode materials. Unexpectedly, however, battery materials display
 376 a partial charge distribution, implying that their charging mechanism must include a
 377 pseudocapacitive contribution. This last point is crucial, as these two types of materials are
 378 frequently pitted against each other in the scientific literature. Nonetheless, we demonstrate
 379 herein, for the first time, that by using our inclusive model one sees a strong connection
 380 between these two types of materials and can observe the source of this distinction. This is
 381 achieved by associating the redox potential distribution model with an experimentally
 382 exploitable electrochemical signal.

383 **Using the quantification of redox potential distribution to determine the electrochemical**
 384 **behavior of Faradaic electrode materials**

385 Based on the probabilistic description of electron exchange through many redox centers,
 386 it is then necessary to create a model that incorporates the redox potential distributions of the
 387 electrochemical signals.

388 In this case, the signal would be the sum of the individual signals from n populations of
 389 redox centers, n being the variable developed in the previous section, *i.e.*, the number of
 390 neighbors impacted by the redox reaction of the so-called standard redox center. In a similar
 391 way to the EDLC current and the battery current, the current resulting from a pseudocapacitive
 392 contribution is expressed as:

393
$$\varphi_{pseudo} = \sum_{i=0}^{i=n} \frac{E_{pseudo}^f - E_{pseudo}^i}{\varepsilon} \varphi_{pseudo}^i \quad \text{Eq. 8.}$$

394 The contribution of the neighbor i would then be similar to the mathematical expression of the
 395 pure battery current as follows:

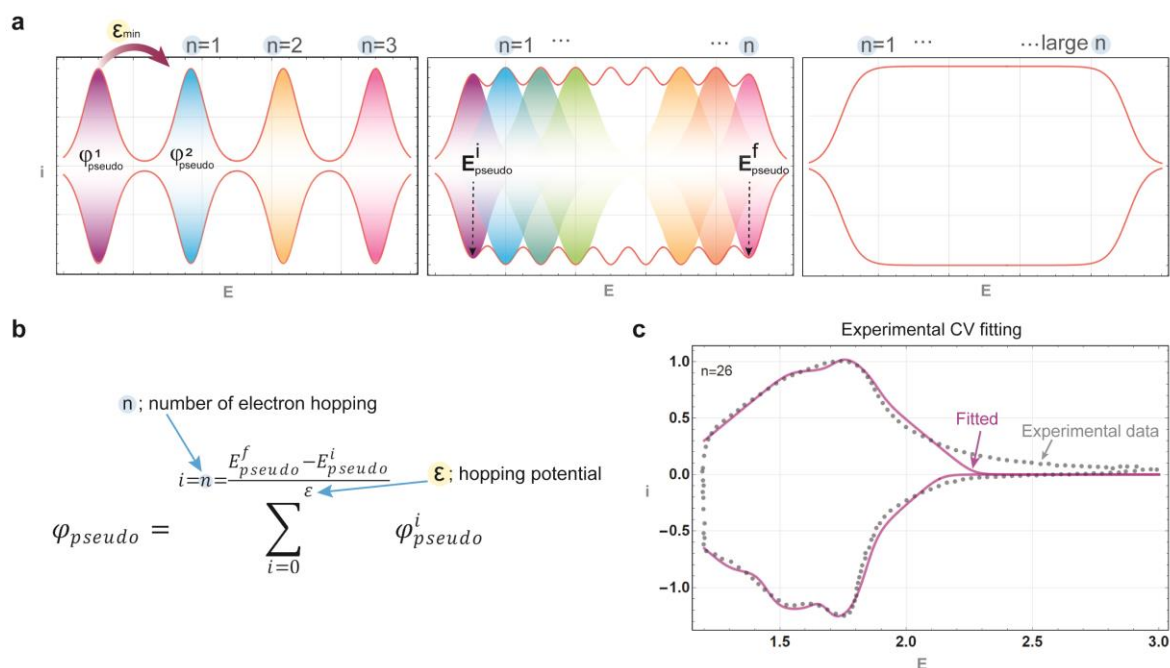
$$396 \quad \varphi_{pseudo}^i = \frac{R \cdot T}{2 \cdot F \cdot G} \cdot e^{\frac{F}{R \cdot T} (E_{apply} - (E_{pseudo}^i + n\varepsilon))} \left(\frac{e^{\frac{F \cdot G}{R \cdot T}}}{1 + e^{\frac{F \cdot G_{pseudo}}{R \cdot T}} \cdot e^{\frac{F}{R \cdot T} (E_{apply} - (E_{pseudo}^i + n\varepsilon))}} - \frac{e^{\frac{-F \cdot G}{R \cdot T}}}{1 + e^{\frac{-F \cdot G}{R \cdot T}} \cdot e^{\frac{F}{R \cdot T} (E_{apply} - (E_{pseudo}^i + n\varepsilon))}} \right) \text{Eq.9,}$$

397 where n is the number of potential hopping between redox centers (per nm³), ε is the hopping
 398 potential (in V), E_{pseudo}^i is the standard redox potential of the pseudocapacitive current (in V),
 399 E_{pseudo}^f is the final potential of the pseudocapacitive current (in V), and φ_{pseudo}^i is the
 400 neighboring pseudocapacitive current (dimensionless current). For the first time, herein we
 401 thus propose a homogeneous and universal formalism for simulating a voltammogram,
 402 irrespective of the origin of its redox dynamics, for all electrochemical energy storage
 403 materials, be they electrochemical double layer, purely battery-type or pseudocapacitive in
 404 nature. Moreover, via this formalism, we can show that all electrode materials possess a
 405 combination of these three contributions. However, the contribution of each of the components
 406 will then be more or less intense, depending on the value of the maximum current (i_{EDLC}^{max} ,
 407 i_{pseudo}^{max} , i_{batt}^{max}), *i.e.*:

$$408 \quad i_{tot} = i_{EDLC}^{max} \cdot \varphi_{EDLC} + i_{pseudo}^{max} \cdot \varphi_{pseudo} + i_{batt}^{max} \cdot \varphi_{batt} \quad \text{Eq.10.}$$

410 **Fig. S11** shows CV profiles of various electrochemical systems, including $i_{peak} +$
 411 i_{EDLC} , pure i_{pseudo} , $i_{pseudo} + i_{EDLC}$, and the contour plots of % pseudo of these systems related
 412 to the resistance and scan rate. These results were obtained by using the Wolfram Language
 413 with its Mathematica tool to plot the functions according to the equation **Eq. 10**, where $A_{batt} =$
 414 $A_{EDLC} = A_{pseudo} = 1$ was considered. Firstly, the different current profiles of the first two
 415 models in **Fig. S11a** and **b**, with different values for R_s and ν , can be observed. These
 416 characteristics relate to different %*pseudo* as indicated in the contour plot (**Fig. S11c**). One can
 417 clearly see that, even when increasing the scan rate, the %*pseudo* still barely reaches 90% as a

418 result of the peak current contribution. This result agrees with experimental observations (see
 419 the ESI). Secondly, the rectangular CV profile (**Fig. S11d** and **e**) is distorted by the presence
 420 of i_{EDLC} current with a large $R_s = 50\Omega$. Similarly, **Fig. S11f** demonstrates %pseudo as a
 421 function of the R_s and the scan rate for a pseudocapacitive current with the contribution of
 422 i_{EDLC} . It was found that the %pseudo is high, even when increasing the scan rate. This result
 423 also agrees with experimental observations (Fig. S13-S60).



424

425 **Fig. 4** | Formalism of the novel pseudocapacitor CV fitting method. (a) Pseudocapacitor CV
 426 of various numbers of electron hopping (or the number of redox centers, n) and the potential
 427 distribution (or hopping potential, ϵ). (b) The equation of pseudocapacitor signal. (c)
 428 Experimental CV fitted by our formalism.

429

430 Fig. 4a shows the proposed pseudocapacitor model where the redox peaks start to overlap with
 431 the number of electron hopping. The extended formalism from **Eq. 8** (as demonstrated in **Fig.**
 432 **4b**) was finally introduced into the total current with other current components (Eq. 10). Using
 433 this model, an experimental CV was well fitted, as shown in **Fig. 4c**. It was also found that,

434 even in the battery materials, there is a certain pseudocapacitive contribution resulting from the
435 distribution of the potential to the nearby redox centers when the number of redox centers per
436 nm^3 is high, as presented in the corresponding matrix models with numerous redox centers
437 (Fig. S13-S60).

438 The conventional method is to use the peak current to determine whether a device is a
439 battery or a pseudocapacitor. While the peak current model is a good fit, the signal including
440 all potential ranges is incomplete. Moreover, the model proposed herein has shown a strong
441 correlation between state-of-the-art experience and reliable theory. Besides, this proposed
442 theory is based on equilibrium exchange between two redox centers, so it cannot be used to
443 analyse the reversibility of the charge-discharge process.

444 **Conclusion**

445 Batteries and supercapacitors are both widely used electrochemical energy storage
446 technologies. When it comes to batteries, redox processes display unusual electrochemical
447 behavior, for which there is no clear explanation to date. Complicating matters further, no
448 universal analytical formalism for assessing voltammograms has thus far been proposed. This
449 article began by discussing the electrochemical properties of batteries and pseudocapacitive
450 materials, as well as what sets them apart while focusing on electron transport pathways. We
451 have shown that battery and pseudocapacitor materials, called Faradaic electrode materials,
452 both exhibit strong electron delocalization resulting in large redox potential distributions due
453 to tunneling and the polaron effect. Perhaps more significantly, battery materials display the
454 same potential dispersion, albeit weaker. Faradaic electrode materials are very much in the
455 scientific limelight of late, and our research serves to provide a link between them all, thereby
456 culminating in a ground-breaking, all-inclusive model for assessing such materials.

457

459 **Reference**

- 460 1. Simon, P.; Gogotsi, Y., Perspectives for electrochemical capacitors and related devices.
461 *Nat Mater* **2020**, *19* (11), 1151-1163.
- 462 2. Ando, Y.; Okubo, M.; Yamada, A.; Otani, M., Capacitive versus Pseudocapacitive
463 Storage in MXene. *Advanced Functional Materials* **2020**, *30* (47).
- 464 3. Augustyn, V.; Simon, P.; Dunn, B., Pseudocapacitive oxide materials for high-rate
465 electrochemical energy storage. *Energy & Environmental Science* **2014**, *7* (5).
- 466 4. Come, J.; Augustyn, V.; Kim, J. W.; Rozier, P.; Taberna, P.-L.; Gogotsi, P.; Long, J.
467 W.; Dunn, B.; Simon, P., Electrochemical Kinetics of Nanostructured Nb₂O₅ Electrodes.
468 *Journal of The Electrochemical Society* **2014**, *161* (5), A718-A725.
- 469 5. Come, J.; Taberna, P. L.; Hamelet, S.; Masquelier, C.; Simon, P., Electrochemical
470 Kinetic Study of LiFePO₄ Using Cavity Microelectrode. *Journal of The Electrochemical*
471 *Society* **2011**, *158* (10).
- 472 6. Costentin, C.; Porter, T. R.; Saveant, J. M., How Do Pseudocapacitors Store Energy?
473 Theoretical Analysis and Experimental Illustration. *ACS Appl Mater Interfaces* **2017**, *9* (10),
474 8649-8658.
- 475 7. Choi, C.; Ashby, D. S.; Butts, D. M.; DeBlock, R. H.; Wei, Q.; Lau, J.; Dunn, B.,
476 Achieving high energy density and high power density with pseudocapacitive materials. *Nature*
477 *Reviews Materials* **2019**, *5* (1), 5-19.
- 478 8. Brousse, T.; Bélanger, D.; Long, J. W., To Be or Not To Be Pseudocapacitive? *Journal*
479 *of The Electrochemical Society* **2015**, *162* (5), A5185-A5189.
- 480 9. M. Toupin, T. Brousse., D. Bélanger, Charge storage mechanism of MnO₂ electrode
481 used in aqueous electrochemical capacitor. *Chem. Mater.* **2004**, *16*, 3184–3190.
- 482 10. Liu, T.; Finn, L.; Yu, M.; Wang, H.; Zhai, T.; Lu, X.; Tong, Y.; Li, Y., Polyaniline and
483 polypyrrole pseudocapacitor electrodes with excellent cycling stability. *Nano Lett* **2014**, *14* (5),
484 2522-7.
- 485 11. A.Aegerter, M., Sol–gel niobium pentoxide: A promising material for electrochromic
486 coatings, batteries, nanocrystalline solar cells and catalysis. *Solar Energy Materials and Solar*
487 *Cells* **2001**, *68* (3-4), 401-422.
- 488 12. Arias, C. R.; Debiemme-Chouvy, C.; Gabrielli, C.; Laberty-Robert, C.; Pailleret, A.;
489 Perrot, H.; Sel, O., New Insights into Pseudocapacitive Charge-Storage Mechanisms in Li-
490 Birnessite Type MnO₂ Monitored by Fast Quartz Crystal Microbalance Methods. *The Journal*
491 *of Physical Chemistry C* **2014**, *118* (46), 26551-26559.
- 492 13. Chen, D.; Ding, D.; Li, X.; Waller, G. H.; Xiong, X.; El-Sayed, M. A.; Liu, M., Probing
493 the Charge Storage Mechanism of a Pseudocapacitive MnO₂ Electrode Using in Operando
494 Raman Spectroscopy. *Chemistry of Materials* **2015**, *27* (19), 6608-6619.
- 495 14. Chigane, M. I., M. , Manganese Oxide Thin Film Preparation by Potentiostatic
496 Electrolyses and Electrochromism. *J. Electrochem. Soc.* **2000**, *147*, 2246
- 497 15. Cong, S.; Tian, Y.; Li, Q.; Zhao, Z.; Geng, F., Single-crystalline tungsten oxide
498 quantum dots for fast pseudocapacitor and electrochromic applications. *Adv Mater* **2014**, *26*
499 (25), 4260-7.

- 500 16. Ganeshan, K.; Shin, Y. K.; Osti, N. C.; Sun, Y.; Prenger, K.; Naguib, M.; Tyagi, M.;
501 Mamontov, E.; Jiang, D. E.; van Duin, A. C. T., Structure and Dynamics of Aqueous
502 Electrolytes Confined in 2D-TiO₂/Ti₃C₂T₂ MXene Heterostructures. *ACS Appl Mater*
503 *Interfaces* **2020**, *12* (52), 58378-58389.
- 504 17. Jabeen, N.; Xia, Q.; Savilov, S. V.; Aldoshin, S. M.; Yu, Y.; Xia, H., Enhanced
505 Pseudocapacitive Performance of alpha-MnO₂ by Cation Preinsertion. *ACS Appl Mater*
506 *Interfaces* **2016**, *8* (49), 33732-33740.
- 507 18. Jadon, A.; Prabhudev, S.; Buvat, G.; Patnaik, S. G.; Djafari-Rouhani, M.; Estève, A.;
508 Guay, D.; Pech, D., Rethinking Pseudocapacitance: A Way to Harness Charge Storage of
509 Crystalline RuO₂. *ACS Applied Energy Materials* **2020**, *3* (5), 4144-4148.
- 510 19. Ji, X.; Xu, K.; Chen, C.; Zhang, B.; Ruan, Y.; Liu, J.; Miao, L.; Jiang, J., Probing the
511 electrochemical capacitance of MXene nanosheets for high-performance pseudocapacitors.
512 *Phys Chem Chem Phys* **2016**, *18* (6), 4460-7.
- 513 20. Juodkazis, K.; Juodkazytė, J.; Šukienė, V.; Griguzevičienė, A.; Selskis, A., On the
514 charge storage mechanism at RuO₂/0.5 M H₂SO₄ interface. *Journal of Solid State*
515 *Electrochemistry* **2007**, *12* (11), 1399-1404.
- 516 21. Lee, C. Y.; Bond, A. M., Revelation of multiple underlying RuO₂ redox processes
517 associated with pseudocapacitance and electrocatalysis. *Langmuir* **2010**, *26* (20), 16155-62.
- 518 22. Lee, M.-T.; Tsai, W.-T.; Deng, M.-J.; Cheng, H.-F.; Sun, I. W.; Chang, J.-K.,
519 Pseudocapacitance of MnO₂ originates from reversible insertion/desertion of thiocyanate
520 anions studied using in situ X-ray absorption spectroscopy in ionic liquid electrolyte. *Journal*
521 *of Power Sources* **2010**, *195* (3), 919-922.
- 522 23. Leong, Z. Y.; Yang, H. Y., A Study of MnO₂ with Different Crystalline Forms for
523 Pseudocapacitive Desalination. *ACS Appl Mater Interfaces* **2019**, *11* (14), 13176-13184.
- 524 24. Liu, Y.; Zhou, F.; Ozolins, V., Ab Initio Study of the Charge-Storage Mechanisms in
525 RuO₂-Based Electrochemical Ultracapacitors. *The Journal of Physical Chemistry C* **2011**, *116*
526 (1), 1450-1457.
- 527 25. Llordes, A.; Garcia, G.; Gazquez, J.; Milliron, D. J., Tunable near-infrared and visible-
528 light transmittance in nanocrystal-in-glass composites. *Nature* **2013**, *500* (7462), 323-6.
- 529 26. Lukatskaya, M. R.; Bak, S.-M.; Yu, X.; Yang, X.-Q.; Barsoum, M. W.; Gogotsi, Y.,
530 Probing the Mechanism of High Capacitance in 2D Titanium Carbide Using In Situ X-Ray
531 Absorption Spectroscopy. *Advanced Energy Materials* **2015**, *5* (15).
- 532 27. Sakai, N.; Ebina, Y.; Takada, K. & Sasaki, T., Electrochromic Films Composed of
533 MnO₂ Nanosheets with Controlled Optical Density and High Coloration Efficiency. *J.*
534 *Electrochem. Soc.* **2005**, *152*.
- 535 28. Scherer, M. R.; Li, L.; Cunha, P. M.; Scherman, O. A.; Steiner, U., Enhanced
536 electrochromism in gyroid-structured vanadium pentoxide. *Adv Mater* **2012**, *24* (9), 1217-21.
- 537 29. Shao, H.; Xu, K.; Wu, Y.-C.; Iadecola, A.; Liu, L.; Ma, H.; Qu, L.; Raymundo-Piñero,
538 E.; Zhu, J.; Lin, Z.; Taberna, P.-L.; Simon, P., Unraveling the Charge Storage Mechanism of
539 Ti₃C₂T_x MXene Electrode in Acidic Electrolyte. *ACS Energy Letters* **2020**, *5* (9), 2873-2880.
- 540 30. Sopčić, S.; Roković, M. K.; Mandić, Z.; Róka, A.; Inzelt, G., Mass changes
541 accompanying the pseudocapacitance of hydrous RuO₂ under different experimental
542 conditions. *Electrochimica Acta* **2011**, *56* (10), 3543-3548.

- 543 31. Sun, P.; Deng, Z.; Yang, P.; Yu, X.; Chen, Y.; Liang, Z.; Meng, H.; Xie, W.; Tan, S.;
544 Mai, W., Freestanding CNT–WO₃ hybrid electrodes for flexible asymmetric supercapacitors.
545 *Journal of Materials Chemistry A* **2015**, *3* (22), 12076-12080.
- 546 32. Tian, Y.; Cong, S.; Su, W.; Chen, H.; Li, Q.; Geng, F.; Zhao, Z., Synergy of W18O₄₉
547 and polyaniline for smart supercapacitor electrode integrated with energy level indicating
548 functionality. *Nano Lett* **2014**, *14* (4), 2150-6.
- 549 33. Watanabe, E.; Ushiyama, H.; Yamashita, K.; Morikawa, Y.; Asakura, D.; Okubo, M.;
550 Yamada, A., Charge Storage Mechanism of RuO₂/Water Interfaces. *The Journal of Physical*
551 *Chemistry C* **2017**, *121* (35), 18975-18981.
- 552 34. Wei, D.; Scherer, M. R.; Bower, C.; Andrew, P.; Ryhanen, T.; Steiner, U., A
553 nanostructured electrochromic supercapacitor. *Nano Lett* **2012**, *12* (4), 1857-62.
- 554 35. Wei, Q.; Liu, J.; Feng, W.; Sheng, J.; Tian, X.; He, L.; An, Q.; Mai, L., Hydrated
555 vanadium pentoxide with superior sodium storage capacity. *Journal of Materials Chemistry A*
556 **2015**, *3* (15), 8070-8075.
- 557 36. Wojtek Dmowski, T. E., Karen E. Swider-Lyons, Corey T. Love, and Debra R. Rolison,
558 Local Atomic Structure and Conduction Mechanism of Nanocrystalline Hydrrous RuO₂ from
559 X-ray Scattering. *J. Phys. Chem. B*.
- 560 37. Xie, Z.; Jin, X.; Chen, G.; Xu, J.; Chen, D.; Shen, G., Integrated smart electrochromic
561 windows for energy saving and storage applications. *Chem Commun (Camb)* **2014**, *50* (5), 608-
562 10.
- 563 38. Yang, P.; Sun, P.; Chai, Z.; Huang, L.; Cai, X.; Tan, S.; Song, J.; Mai, W., Large-scale
564 fabrication of pseudocapacitive glass windows that combine electrochromism and energy
565 storage. *Angew Chem Int Ed Engl* **2014**, *53* (44), 11935-9.
- 566 39. Yang, P.; Sun, P.; Du, L.; Liang, Z.; Xie, W.; Cai, X.; Huang, L.; Tan, S.; Mai, W.,
567 Quantitative Analysis of Charge Storage Process of Tungsten Oxide that Combines
568 Pseudocapacitive and Electrochromic Properties. *The Journal of Physical Chemistry C* **2015**,
569 *119* (29), 16483-16489.
- 570 40. Yang, P.; Sun, P.; Mai, W., Electrochromic energy storage devices. *Materials Today*
571 **2016**, *19* (7), 394-402.
- 572 41. Yoshida, N.; Yamada, Y.; Nishimura, S.-i.; Oba, Y.; Ohnuma, M.; Yamada, A.,
573 Unveiling the Origin of Unusual Pseudocapacitance of RuO₂·nH₂O from Its Hierarchical
574 Nanostructure by Small-Angle X-ray Scattering. *The Journal of Physical Chemistry C* **2013**,
575 *117* (23), 12003-12009.
- 576 42. Zhan, C.; Jiang, D. E., Understanding the pseudocapacitance of RuO₂ from joint
577 density functional theory. *J Phys Condens Matter* **2016**, *28* (46), 464004.
- 578 43. Zhan, C.; Naguib, M.; Lukatskaya, M.; Kent, P. R. C.; Gogotsi, Y.; Jiang, D. E.,
579 Understanding the MXene Pseudocapacitance. *J Phys Chem Lett* **2018**, *9* (6), 1223-1228.
- 580 44. Zhu, Y.-P.; Xia, C.; Lei, Y.; Singh, N.; Schwingenschlögl, U.; Alshareef, H. N.,
581 Solubility contrast strategy for enhancing intercalation pseudocapacitance in layered MnO₂
582 electrodes. *Nano Energy* **2019**, *56*, 357-364.
- 583 45. Bhagwan, J.; Kumar, N.; Yadav, K. L.; Sharma, Y., Probing the electrical properties
584 and energy storage performance of electrospun ZnMn₂O₄ nanofibers. *Solid State Ionics* **2018**,
585 *321*, 75-82.

- 586 46. Blidberg, A.; Gustafsson, T.; Tengstedt, C.; Björefors, F.; Brant, W. R., Monitoring
587 $\text{Li}_x\text{FeSO}_4\text{F}$ ($x = 1, 0.5, 0$) Phase Distributions in Operando To Determine Reaction
588 Homogeneity in Porous Battery Electrodes. *Chemistry of Materials* **2017**, *29* (17), 7159-7169.
- 589 47. Chen, Z.; Xu, F.; Cao, S.; Li, Z.; Yang, H.; Ai, X.; Cao, Y., High Rate, Long Lifespan
590 LiV_3O_8 Nanorods as a Cathode Material for Lithium-Ion Batteries. *Small* **2017**, *13* (18).
- 591 48. Dong, R.; Ye, Q.; Kuang, L.; Lu, X.; Zhang, Y.; Zhang, X.; Tan, G.; Wen, Y.; Wang,
592 F., Enhanced supercapacitor performance of Mn_3O_4 nanocrystals by doping transition-metal
593 ions. *ACS Appl Mater Interfaces* **2013**, *5* (19), 9508-16.
- 594 49. Drozhzhin, O. A.; Tertov, I. V.; Alekseeva, A. M.; Aksyonov, D. A.; Stevenson, K. J.;
595 Abakumov, A. M.; Antipov, E. V., $\beta\text{-NaVP}_2\text{O}_7$ as a Superior Electrode Material for Na-Ion
596 Batteries. *Chemistry of Materials* **2019**, *31* (18), 7463-7469.
- 597 50. Du, J.; Jiao, L.; Wu, Q.; Liu, Y.; Zhao, Y.; Guo, L.; Wang, Y.; Yuan, H., Synthesis and
598 characterization of $\text{Li}_2\text{FeP}_2\text{O}_7/\text{C}$ nanocomposites as cathode materials for Li-ion batteries.
599 *Electrochimica Acta* **2013**, *103*, 219-225.
- 600 51. Geng, X.; Zhang, Y.; Han, Y.; Li, J.; Yang, L.; Benamara, M.; Chen, L.; Zhu, H., Two-
601 Dimensional Water-Coupled Metallic MoS_2 with Nanochannels for Ultrafast Supercapacitors.
602 *Nano Lett* **2017**, *17* (3), 1825-1832.
- 603 52. Goikolea, E.; Daffos, B.; Taberna, P. L.; Simon, P., Synthesis of nanosized MnO_2
604 prepared by the polyol method and its application in high power supercapacitors. *Materials for*
605 *Renewable and Sustainable Energy* **2013**, *2* (3-4).
- 606 53. Guo, D.; Zhang, H.; Yu, X.; Zhang, M.; Zhang, P.; Li, Q.; Wang, T., Facile synthesis
607 and excellent electrochemical properties of CoMoO_4 nanoplate arrays as supercapacitors.
608 *Journal of Materials Chemistry A* **2013**, *1* (24).
- 609 54. He, D.; Wu, T.; Wang, B.; Yang, Y.; Zhao, S.; Wang, J.; Yu, H., Novel $\text{Na}_2\text{TiSiO}_5$
610 anode material for lithium ion batteries. *Chem Commun (Camb)* **2019**, *55* (15), 2234-2237.
- 611 55. Inamdar, A. I.; Ahmed, A. T. A.; Chavan, H. S.; Jo, Y.; Cho, S.; Kim, J.; Pawar, S. M.;
612 Hou, B.; Cha, S.; Kim, H.; Im, H., Influence of operating temperature on $\text{Li}_2\text{ZnTi}_3\text{O}_8$ anode
613 performance and high-rate charging activity of Li-ion battery. *Ceramics International* **2018**,
614 *44* (15), 18625-18632.
- 615 56. Jang, H.; Jin, W.; Nam, G.; Yoo, Y.; Jeon, J. S.; Park, J.; Kim, M. G.; Cho, J., Exploring
616 the artificially induced nonstoichiometric effect of Li_2RuO_3 as a reactive promoter on
617 electrocatalytic behavior. *Energy & Environmental Science* **2020**, *13* (7), 2167-2177.
- 618 57. Jenkins, T.; Alarco, J. A.; Mackinnon, I. D. R., Synthesis and Characterization of a
619 Novel Hydrated Layered Vanadium(III) Phosphate Phase $\text{K}_3\text{V}_3(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$: A Functional
620 Cathode Material for Potassium-Ion Batteries. *ACS Omega* **2021**, *6* (3), 1917-1929.
- 621 58. Kim, J. W.; Augustyn, V.; Dunn, B., The Effect of Crystallinity on the Rapid
622 Pseudocapacitive Response of Nb_2O_5 . *Advanced Energy Materials* **2012**, *2* (1), 141-148.
- 623 59. Kwon, N. H.; Yin, H.; Vavrova, T.; Lim, J. H. W.; Steiner, U.; Grobety, B.; Fromm, K.
624 M., Nanoparticle shapes of LiMnPO_4 , Li^+ diffusion orientation and diffusion coefficients for
625 high volumetric energy Li^+ ion cathodes. *Journal of Power Sources* **2017**, *342*, 231-240.
- 626 60. Lu, J.; Ran, H.; Li, J.; Wan, J.; Wang, C.; Ji, P.; Wang, X.; Liu, G.; Hu, C., A fast
627 composite-hydroxide-mediated approach for synthesis of 2D- LiCoO_2 for high performance
628 asymmetric supercapacitor. *Electrochimica Acta* **2020**, *331*.

- 629 61. Lu, X.; Yu, M.; Zhai, T.; Wang, G.; Xie, S.; Liu, T.; Liang, C.; Tong, Y.; Li, Y., High
630 energy density asymmetric quasi-solid-state supercapacitor based on porous vanadium nitride
631 nanowire anode. *Nano Lett* **2013**, *13* (6), 2628-33.
- 632 62. Lukatskaya, M. R. e. a., Cation Intercalation and High Volumetric Capacitance of Two-
633 Dimensional Titanium Carbide. *Science* **2013**, *341*, 1502–1505.
- 634 63. Malaie, K.; Scholz, F., Realizing alkaline all-pseudocapacitive supercapacitors based
635 on highly stable nanospinel oxide coatings. *Colloids and Surfaces A: Physicochemical and*
636 *Engineering Aspects* **2019**, *577*, 576-582.
- 637 64. Mu, J.; Wang, J.; Hao, J.; Cao, P.; Zhao, S.; Zeng, W.; Miao, B.; Xu, S., Hydrothermal
638 synthesis and electrochemical properties of V₂O₅ nanomaterials with different dimensions.
639 *Ceramics International* **2015**, *41* (10), 12626-12632.
- 640 65. Nithya, V. D.; Pandi, K.; Lee, Y. S.; Selvan, R. K., Synthesis, characterization and
641 electrochemical performances of nanocrystalline FeVO₄ as negative and LiCoPO₄ as positive
642 electrode for asymmetric supercapacitor. *Electrochimica Acta* **2015**, *167*, 97-104.
- 643 66. Opitz, M.; Yue, J.; Wallauer, J.; Smarsly, B.; Roling, B., Mechanisms of Charge
644 Storage in Nanoparticulate TiO₂ and Li₄Ti₅O₁₂ Anodes: New Insights from Scan rate-
645 dependent Cyclic Voltammetry. *Electrochimica Acta* **2015**, *168*, 125-132.
- 646 67. Qu, L.; Liu, Y.; Fang, S.; Yang, L.; Hirano, S.-i., Li₂FeSiO₄ coated by sorbitanlaurat-
647 derived carbon as cathode of high-performance lithium-ion battery. *Electrochimica Acta* **2015**,
648 *163*, 123-131.
- 649 68. Rakhi, R. B.; Ahmed, B.; Hedhili, M. N.; Anjum, D. H.; Alshareef, H. N., Effect of
650 Postetch Annealing Gas Composition on the Structural and Electrochemical Properties of
651 Ti₂C_{Tx} MXene Electrodes for Supercapacitor Applications. *Chemistry of Materials* **2015**, *27*
652 (15), 5314-5323.
- 653 69. Rakhi, R. B.; Chen, W.; Cha, D.; Alshareef, H. N., Substrate dependent self-
654 organization of mesoporous cobalt oxide nanowires with remarkable pseudocapacitance. *Nano*
655 *Lett* **2012**, *12* (5), 2559-67.
- 656 70. Sahoo, S.; Ratha, S.; Rout, C. S., Spinel NiCo₂O₄ Nanorods
657 for Supercapacitor Applications. *American Journal of Engineering and Applied Sciences* **2015**,
658 *8* (3), 371-379.
- 659 71. Shafi, P. M.; Joseph, N.; Thirumurugan, A.; Bose, A. C., Enhanced electrochemical
660 performances of agglomeration-free LaMnO₃ perovskite nanoparticles and achieving high
661 energy and power densities with symmetric supercapacitor design. *Chemical Engineering*
662 *Journal* **2018**, *338*, 147-156.
- 663 72. Shan, Q.; Mu, X.; Alhabeab, M.; Shuck, C. E.; Pang, D.; Zhao, X.; Chu, X.-F.; Wei, Y.;
664 Du, F.; Chen, G.; Gogotsi, Y.; Gao, Y.; Dall'Agnese, Y., Two-dimensional vanadium carbide
665 (V₂C) MXene as electrode for supercapacitors with aqueous electrolytes. *Electrochemistry*
666 *Communications* **2018**, *96*, 103-107.
- 667 73. Shen, L.; Chen, S.; Maier, J.; Yu, Y., Carbon-Coated Li₃VO₄ Spheres as Constituents
668 of an Advanced Anode Material for High-Rate Long-Life Lithium-Ion Batteries. *Adv Mater*
669 **2017**, *29* (33).
- 670 74. Singh, P.; Shiva, K.; Celio, H.; Goodenough, J. B., Eldfellite, NaFe(SO₄)₂: an
671 intercalation cathode host for low-cost Na-ion batteries. *Energy & Environmental Science*
672 **2015**, *8* (10), 3000-3005.

- 673 75. Vattikuti, S. V. P.; Devarayapalli, K. C.; Dang, N. N.; Shim, J., 1D/1D
674 Na₂Ti₃O₇/SWCNTs electrode for split-cell-type asymmetric supercapacitor device. *Ceramics*
675 *International* **2021**, *47* (8), 11602-11610.
- 676 76. Vignesh, V.; Subramani, K.; Sathish, M.; Navamathavan, R., Electrochemical
677 investigation of manganese ferrites prepared via a facile synthesis route for supercapacitor
678 applications. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2018**, *538*,
679 668-677.
- 680 77. Vincent, R. C.; Vishnoi, P.; Preefer, M. B.; Shen, J. X.; Seeler, F.; Persson, K. A.;
681 Seshadri, R., Li₅VF₄(SO₄)₂: A Prototype High-Voltage Li-Ion Cathode. *ACS Appl Mater*
682 *Interfaces* **2020**, *12* (43), 48662-48668.
- 683 78. Vujković, M.; Mitrić, M.; Mentus, S., High-rate intercalation capability of NaTi₂(PO
684 ₄)₃/C composite in aqueous lithium and sodium nitrate solutions. *Journal of Power Sources*
685 **2015**, *288*, 176-186.
- 686 79. Wang, D.; Xiao, J.; Xu, W.; Nie, Z.; Wang, C.; Graff, G.; Zhang, J.-G., Preparation and
687 electrochemical investigation of Li₂CoPO₄F cathode material for lithium-ion batteries.
688 *Journal of Power Sources* **2011**, *196* (4), 2241-2245.
- 689 80. Whiteley, Justin M.; Hafner, S.; Han, S. S.; Kim, S. C.; Le, V.-D.; Ban, C.; Kim, Y. H.;
690 Oh, K. H.; Lee, S.-H., All-solid-state disordered LiTiS₂pseudocapacitor. *Journal of Materials*
691 *Chemistry A* **2017**, *5* (30), 15661-15668.
- 692 81. Wu, C.; Wu, Z. G.; Zhang, X.; Rajagopalan, R.; Zhong, B.; Xiang, W.; Chen, M.; Li,
693 H.; Chen, T.; Wang, E.; Yang, Z.; Guo, X., Insight into the Origin of Capacity Fluctuation of
694 Na₂Ti₆O₁₃ Anode in Sodium Ion Batteries. *ACS Appl Mater Interfaces* **2017**, *9* (50), 43596-
695 43602.
- 696 82. Xiao, J.; Wen, J.; Zhao, J.; Ma, X.; Gao, H.; Zhang, X., A safe etching route to
697 synthesize highly crystalline Nb₂CT_x MXene for high performance asymmetric supercapacitor
698 applications. *Electrochimica Acta* **2020**, *337*.
- 699 83. Xiao, P. F.; Lai, M. O.; Lu, L., Transport and electrochemical properties of high
700 potential favorite LiVPO₄F. *Solid State Ionics* **2013**, *242*, 10-19.
- 701 84. Xu, H.; Shu, J.; Hu, X.; Sun, Y.; Luo, W.; Huang, Y., Electrospun porous LiNb₃O₈
702 nanofibers with enhanced lithium-storage properties. *Journal of Materials Chemistry A* **2013**,
703 *1* (47).
- 704 85. Xu, W.; Jiang, Z.; Yang, Q.; Huo, W.; Javed, M. S.; Li, Y.; Huang, L.; Gu, X.; Hu, C.,
705 Approaching the lithium-manganese oxides' energy storage limit with Li₂MnO₃ nanorods for
706 high-performance supercapacitor. *Nano Energy* **2018**, *43*, 168-176.
- 707 86. Yang, Y. e. a., Hydrothermally Formed Three-Dimensional Nanoporous Ni(OH)₂
708 Thin-Film Supercapacitors. *Nano Lett.* **2014**, *12*, 2559-2567.
- 709 87. Zhang, J. e. a., Template Synthesis of Tubular Ruthenium Oxides for Supercapacitor
710 Applications. *J. Phys. Chem. C* **2010**, *114*, 13608-13613.
- 711 88. Zhang, Y.; Ding, Z.; Foster, C. W.; Banks, C. E.; Qiu, X.; Ji, X., Oxygen Vacancies
712 Evoked Blue TiO₂(B) Nanobelts with Efficiency Enhancement in Sodium Storage Behaviors.
713 *Advanced Functional Materials* **2017**, *27* (27).
- 714 89. Zhao, G.; Zhang, N.; Sun, K., Porous MoO₃ films with ultra-short relaxation time used
715 for supercapacitors. *Materials Research Bulletin* **2013**, *48* (3), 1328-1332.

- 716 90. Zheng, J.-c.; Han, Y.-d.; Tang, L.-b.; Zhang, B., Investigation of phase structure change
717 and electrochemical performance in LiVP2O7-Li3V2(PO4)3-LiVPO4F system.
718 *Electrochimica Acta* **2016**, *198*, 195-202.
- 719 91. Zhu, H.; He, H.; Xin, X.; Ma, X.; Zan, L.; Zhang, Y., Facile synthesis of
720 Li2MnSiO4/C/graphene composite with superior high-rate performances as cathode materials
721 for Li-ion batteries. *Electrochimica Acta* **2015**, *155*, 116-124.
- 722 92. J.W. Long, K. E. S., C.I. Merzbacher, D.R. Rolison, Voltammetric Characterization of
723 Ruthenium Oxide-Based Aerogels and Other RuO2 Solids: The Nature of Capacitance in
724 Nanostructured Materials. *Langmuir* **1999**, *15*, 780-784.
- 725 93. Sugimoto, W.; Yokoshima, K.; Murakami, Y.; Takasu, Y., Charge storage mechanism
726 of nanostructured anhydrous and hydrous ruthenium-based oxides. *Electrochimica Acta* **2006**,
727 *52* (4), 1742-1748.
- 728 94. Liu, J.; Wang, J.; Ni, Y.; Zhang, K.; Cheng, F.; Chen, J., Recent breakthroughs and
729 perspectives of high-energy layered oxide cathode materials for lithium ion batteries. *Materials*
730 *Today* **2021**, *43*, 132-165.
- 731 95. Kim, H.-J.; Krishna, T. N. V.; Zeb, K.; Rajangam, V.; Gopi, C. V. V. M.; Sambasivam,
732 S.; Raghavendra, K. V. G.; Obaidat, I. M., A Comprehensive Review of Li-Ion Battery
733 Materials and Their Recycling Techniques. *Electronics* **2020**, *9* (7).
- 734 96. Trasatti, S. B., G., A new interesting electrode material. Solid state structure and
735 electrochemical behaviour. *J. Electroanal. Chem.* **1971**, *29*, 4-8.
- 736 97. Marcus, R. A., On the Theory of Electron-Transfer Reactions. VI. Unified Treatment
737 for Homogeneous and Electrode Reactions. *The Journal of Chemical Physics* **1965**, *43* (2),
738 679-701.
- 739 98. <J. M. Savéant, J. Phys. Chem. B, 106 (2002) 9387.pdf>.
- 740 99. Fraggedakis, D.; McEldrew, M.; Smith, R. B.; Krishnan, Y.; Zhang, Y.; Bai, P.; Chueh,
741 W. C.; Shao-Horn, Y.; Bazant, M. Z., Theory of coupled ion-electron transfer kinetics.
742 *Electrochimica Acta* **2021**, 367.
- 743 100. Franchini, C.; Reticcioli, M.; Setvin, M.; Diebold, U., Polarons in materials. *Nature*
744 *Reviews Materials* **2021**, *6* (7), 560-586.
- 745 101. Costentin, C., Electrochemical Energy Storage: Questioning the Popular $v/v(1/2)$ Scan
746 Rate Diagnosis in Cyclic Voltammetry. *J Phys Chem Lett* **2020**, *11* (22), 9846-9849.
- 747 102. Forghani, M.; Donne, S. W., Method Comparison for Deconvoluting Capacitive and
748 Pseudo-Capacitive Contributions to Electrochemical Capacitor Electrode Behavior. *Journal of*
749 *The Electrochemical Society* **2018**, *165* (3), A664-A673.
- 750 103. Chen, G. Z., Linear and non-linear pseudocapacitances with or without diffusion
751 control. *Progress in Natural Science: Materials International* **2021**, *31* (6), 792-800.
- 752 104. Yu, L. P.; Chen, G. Z., Redox electrode materials for supercapatteries. *Journal of Power*
753 *Sources* **2016**, *326* (15), 604-612.
- 754 105. Oh, S. W., Bang, H. J., Bae, Y. C., Sun, Y.-K.; Effect of calcination temperature on
755 morphology, crystallinity and electrochemical properties of nano-crystalline metal oxides
756 (Co3O4, CuO, and NiO) prepared via ultrasonic spray pyrolysis. *Journal of Power Sources*
757 **2007**, *173* (1), 502-509.

- 758 106. Anasori, B., Lukatskaya, M. R., Gogotsi, Y.; 2D metal carbides and nitrides (MXenes)
759 for energy storage. *Nature Reviews Materials* **2017**, 2 (2), 16098.
- 760 107. Hu, M.; Zhang, H.; Hu, T.; Fan, B.; Wang, X.; Li, Z. Emerging 2D MXenes for
761 supercapacitors: status, challenges and prospects. *Chemical Society Reviews* **2020**, 49 (18),
762 6666-6693.
- 763 108. Augustyn, V.; Simon, P.; Dunn, B. Pseudocapacitive oxide materials for high-rate
764 electrochemical energy storage. *Energy & Environmental Science* **2014**, 7 (5), 1597-1614.
- 765 109. Jiang, Y.; Liu, J. Definitions of Pseudocapacitive Materials: A Brief Review. *ENERGY*
766 & *ENVIRONMENTAL MATERIALS* **2019**, 2 (1), 30-37.
- 767 110. Choi, C.; Ashby, D. S.; Butts, D. M.; DeBlock, R. H.; Wei, Q.; Lau, J.; Dunn, B.
768 Achieving high energy density and high power density with pseudocapacitive materials. *Nature*
769 *Reviews Materials* **2020**, 5 (1), 5-19.
- 770 111. Li, X.; Huang, Z.; Shuck, C. E.; Liang, G.; Gogotsi, Y.; Zhi, C. MXene chemistry,
771 electrochemistry and energy storage applications. *Nature Reviews Chemistry* **2022**, 6 (6), 389-
772 404.
- 773 112. Dupont, M. F.; Donne, S. W. Charge storage mechanisms in electrochemical capacitors:
774 Effects of electrode properties on performance. *Journal of Power Sources* 2016, 326, 613-623.
- 775 113. Forghani, M.; Donne, S. W. Method Comparison for Deconvoluting Capacitive and
776 Pseudo-Capacitive Contributions to Electrochemical Capacitor Electrode Behavior. *Journal of*
777 *The Electrochemical Society* 2018, 165 (3), A664-A673.
- 778 114. Fleischmann, S.; Zhang, Y.; Wang, X.; Cummings, P. T.; Wu, J.; Simon, P.; Gogotsi,
779 Y.; Presser, V.; Augustyn, V. Continuous transition from double-layer to Faradaic charge
780 storage in confined electrolytes. *Nature Energy* 2022, 7 (3), 222-228.
- 781 115. Deebansok, S.; Deng, J.; Le Calvez, E.; Zhu, Y.; Crosnier, O.; Brousse, T.; Fontaine,
782 O. Capacitive tendency concept alongside supervised machine-learning toward classifying
783 electrochemical behavior of battery and pseudocapacitor materials. *Nature Communications*
784 **2024**, 15 (1), 1133. DOI: 10.1038/s41467-024-45394-w.
- 785 116. Wang, J.; Polleux, J.; Lim, J.; Dunn, B. Pseudocapacitive Contributions to
786 Electrochemical Energy Storage in TiO₂ (Anatase) Nanoparticles. *The Journal of Physical*
787 *Chemistry C* **2007**, 111 (40), 14925-14931. DOI: 10.1021/jp074464w.