

Supporting Information

Energy Storage. Pseudocapacitance in Prospect

Cyrille Costentin* and Jean-Michel Savéant*

1. Two picturesque albeit fanciful descriptions of the construction of a “pseudocapacitance” from Faradaic reactions.

Figure S1 nicely summarizes the construction of a “pseudocapacitance” from faradaic reactions in the case of MnO₂ in reference S1. The eight vertical ellipses stand for the CV responses of eight partial surface fast reversible faradaic reactions (eligible each to the application of Nernst law), whose sum would reproduce the experimental CV response of this material.

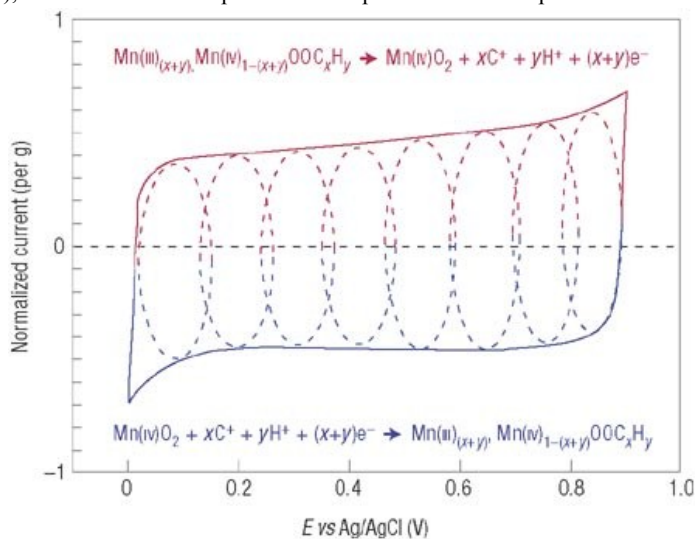


Fig. S1. Reproduction of figure 6 in reference S1 with the legend: “Cyclic voltammetry. This schematic of cyclic voltammetry for a MnO₂-electrode cell in mild aqueous electrolyte (0.1 M K₂SO₄) shows the successive multiple surface redox reactions leading to the pseudo-capacitive charge storage mechanism. The red (upper) part is related to the oxidation from Mn(III) to Mn(IV) and the blue (lower) part refers to the reduction from Mn(IV) to Mn(III)”, with permission.

A first remark is that application of Nernst law to these eight surface redox couples would certainly not lead to vertical ellipses but to the thin reversible peaks represented in figure 1b. Then, why eight couples? Why equal probabilities for each? In fact a serious

analysis, absent from this nice-looking cartoon, would lend back to the same analysis as in the text with the same unavoidable conclusion that the apparent capacitance thus obtained cannot be confounded with the expected quasi-rectangular response.

Even more breath-taking cartoons are available from reference S2 (figure S3). Not a single indication is given about the values (even as orders of magnitude) of the standard potentials of the various redox couples involved! The same for their respective probabilities in the construction of the “pseudocapacitance”, which is left to the reader’s fantasy. In total, no analysis, just another piece of science fiction! The danger of such eye-catching no-substance reports is that they could misleadingly draw fresh readers to the completely erroneous impression that “pseudocapacitors” do exist and that “pseudocapacitance” is a valid notion.

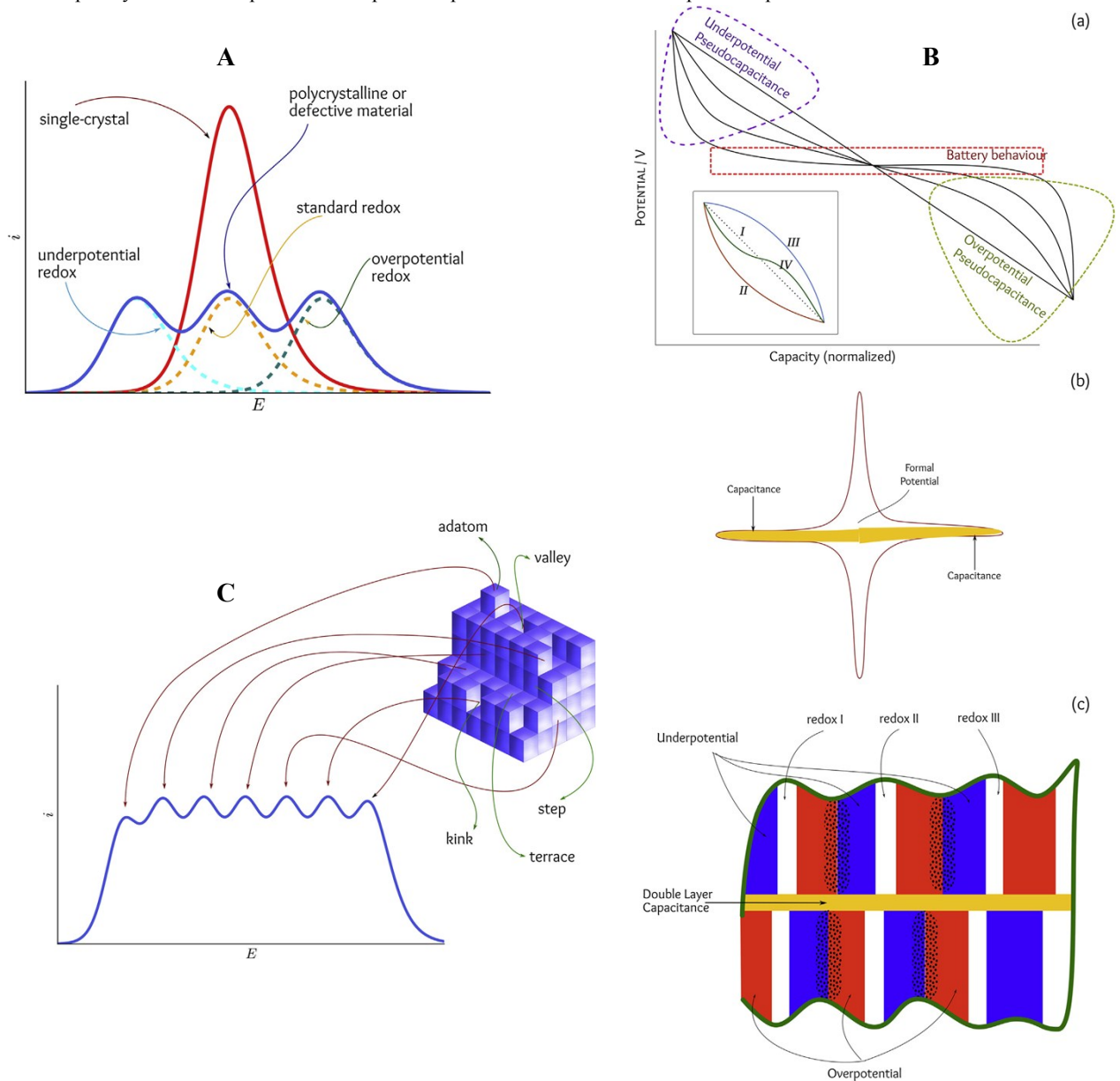


Fig. S2. from figures 2, 5 & 8 in reference 12, with permission. **A.** An illustrative model of the voltammetric behavior of a metal oxide where some underpotential and overpotential redox sites exist along with the standard redox sites. The red curve represents a perfect single-crystalline material in which all the redox sites have the formal redox potential. The solid blue line depicts a case where only 1/3 of the redox sites react at the standard potential, and 1/3 reacts at x V below the standard potential (in the underpotential region) and 1/3 at x V above the standard potential (in the overpotential region). The dashed lines indicate the individual voltammograms where only the corresponding redox sites were active in the system. **B:** Transition from battery to pseudocapacitive behavior. (a) Charge/discharge profiles: The x-axis has been normalized for the maximum capacity achieved in each case. (b) Cyclic voltammogram of a battery material. (c) Illustrating the contributions of underpotential and overpotential processes in respect to the redox systems, creating a capacitive like behavior. In this case, three redox systems are shown in which the peak is broadened by underpotential and overpotential regions. In other words, this CV is the combination of three CVs presented in A. **C:** A schematic illustration of common surface defects and their influence on broadening the voltammetric peak via small redox peaks.

2. “Modelling pseudo capacitance of manganese dioxide” (from reference S3). A remarkably tautological approach of pseudocapacitance

The model offered here to explain why and how faradaic reactions may give rise to a purely capacitive response starts in a similar manner as Conway’s detailed in Section 3 of the main text. Similar, but not quite the same. As in Conway’s the current-potential response is viewed as resulting from the summation of a set of elementary Faradaic reactions. One difference is that the kinetics of each elementary Faradaic step is taken into account and assumed to obey the Butler-Volmer law:

$$j_f = j_0 \left\{ \exp\left(\frac{\alpha(U - E_{eq})F}{RT}\right) - \exp\left(\frac{(1-\alpha)(U - E_{eq})F}{RT}\right) \right\} \quad (1)$$

Charge=Increasing oxidation state=Increasing E_{eq}

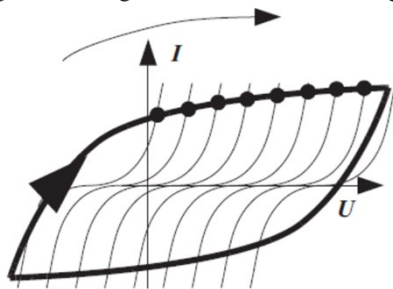


Fig. S3. Reproduction of figure 1 in reference 14, with permission.

associated with coupled diffusion of an ion as the oxidation state of Mn changes. The diffusion is in fact immediately neglected as soon as mentioned. One ends up with the series of rising-descending light curves shown in figure S3. In Conway’s, the Faradaic steps were adsorbed-reactant Nernstian reactions whose weighted summation, which targets a rectangular response, leads to the thickened-peak as already shown and discussed in the text. In the present “model” no such attempt is carried out. The reader has no indication of how the $-\infty$ -to- $+\infty$ thin Butler-Volmer curves should combine to achieve a rectangular-looking CV response. Instead, suddenly, what was expected to be the conclusion of the model becomes an hypothesis (“supposing that during a cyclic voltammetry experiment, the material behaviour is similar to a pure electrical capacity, the relation between the intensity and the voltage variation is described by the fundamental relation: $I = CdU / dt = \pm CV_{sc}$ ”). In other words, a constant current is reached because a constant current is reached. Besides this plain tautology, the rest is made of incoherent playing with improbable equations, introducing new “constants” that cannot be independently defined and estimated and have no reasons to be actually constant.

It is clear that the “models” evoked in the two above sections are much worse than Conway’s treatment. Indeed, if the latter did not succeed to establish the notion of “pseudocapacitance”, at least the derivations it contains were not altered by grossly incorrect algebraic hotchpotches.

References

- (S1). P. Simon and Y. Gogotsi, *Nat Mater*, 2008, **7**, 845-854.
- (S2). A. Eftekhari and M. Mohamedi, *Mater. Today Energ.*, 2017, **6**, 211-229.
- (S3). P. Guillemet, T. Brousse, O. Crosnier, Y. Dandeville, L. Athouel and Y. Scudeller, *Electrochim. Acta*, 2012, **67**, 41-49.