THE CONCEPT OF CHEMICAL CAPACITANCE

A CRITIQUE

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ABSTRACT The concept of chemical capacitance as introduced by Hong and Mauzerall (*Proc. Natl. Acad. Sci. U.S.A. 1974.* **71**:1564) is critically reexamined. This novel capacitance was introduced to explain the time-course of flash-induced photocurrents observed in lipid bilayer membranes containing porphyrins. According to Hong and Mauzerall, the chemical capacitance results from a combination of three fundamental capacitances: the geometric membrane capacitance and the two interfacial double layer capacitances. The concept of chemical capacitance is questioned for the following reasons: (*i*) The system analysis is insufficiently determinate. (*ii*) The measured chemical capacitance is ~ 0.16% of that predicted by the theory. (*iii*) The fact that only 20% of the membrane area is illuminated was not considered in the analysis. The latter point offers an alternative explanation of the capacitance in question: this capacitance may reflect that fraction of the total membrane capacitance that is photochemically active. If so, the concept of chemical capacitance lacks general significance.

INTRODUCTION

In the last ten years considerable attention has been paid to light-induced electrical signals arising from photobiological systems as well as from model systems. Various photopotentials have been reported, for instance from chloroplasts (Witt and Zickler, 1973; Fowler and Kok, 1974; Bulychev and Vredenberg, 1976) or visual photoreceptors (Brown and Murakami, 1964; Cone and Pak, 1971). There has been extensive work done on model systems, such as planar lipid bilayer membranes, doped either with natural dyes (Tien, 1972; Trissl and Läuger, 1972; Schadt, 1973; Fröhlich and Diehn, 1974), synthetic dyes (Verma, 1971; Ullrich and Kuhn, 1972; Duchek and Huebner, 1979), or photosensitive proteins (Roux and Yguerabide, 1973; Montal et al., 1977; Herrmann and Rayfield, 1978; Bamberg et al., 1979; Chen and Berns, 1979; Hong and Montal, 1979). Recently, techniques have been developed to measure interfacial charge displacements with a time resolution on the order of nanoseconds and with a sensitivity of ~ 100 μV (Huebner, 1979; Trissl, 1980; Trissl and Gräber, 1980).

In 1974 Hong and Mauzerall measured flash-induced photocurrents from a lipid bilayer membrane doped with lipid soluble porphyrins. To describe the observed electrical signals, the authors used an equivalent circuit which contained the usual membrane capacitance as well as another called "chemical capacitance." This novel capacitance was presented as a combination of the geometrical membrane capacitance with the two capacitances of the ionic double layers. Although the novel capacitance was detected only in this experimental system, Hong suggested that there could be a basic underlying concept which plays a general and fundamental role in photobiological reactions, specifically in photosynthetic membranes of

chloroplasts, disk membranes of rod outer segments, and purple membranes of halophilic bacteria (Hong, 1976).

This communication reexamines the significance of "chemical capacitance" with respect to the equivalent circuits in question. Theoretical and experimental peculiarities are discussed, and finally, an alternative interpretation is outlined.

THE EXPERIMENTAL SYSTEM

The experimental system which led Hong and Mauzerall (1974) to postulate "chemical capacitance" consisted of a lipid bilayer membrane doped with esters of magnesium-meso porphyrin IX or, alternatively, magnesium octaethylporphyrin (P). These dyes are lipophilic and therefore are located in the membrane. A redox potential gradient across the membrane is adjusted with ferri- and ferrocyanide: ". . . the aqueous phases are made asymmetrical so that one aqueous phase contains predominantly oxidant. . ., while the other aqueous phase contains either no redox reagents or predominantly reductant. . . ." (Hong and Mauzerall, 1974). Stationary photocurrents were measured under steady state illumination, whereas fast photocurrent transients were observed under flash illumination.

The experimental observations could be described by the chemical reactions of the excited porphyrin and the porphyrin cation formed at the two interfaces of the bilayer membrane (Hong and Mauzerall, 1974):

$$\textit{left interface:}\quad P + Fe(CN)_6^{3-} \overset{h \cdot \nu}{\rightleftharpoons} P^+ + Fe(CN)_6^{4-} \tag{1a}$$

$$\textit{right interface:}\quad P^+ + Fe(CN)_6^{4-} \longrightarrow P + Fe(CN)_6^{3-} \tag{1b}$$

A more detailed mechanism has been reported recently by Young and Feldberg (1979). Since, according to Hong and Mauzerall (1974), the ". . . diffusion of P^+ across the membrane is slow. . ., most P^+ reacts with ferrocyanide at the same interface where it was formed." Thus, an electron transfer reaction across a single membrane-water interface is observed as the predominant reaction. The porphyrins are thought to be membrane-bound, whereas the ferri- and ferrocyanide ions are dissolved in the aqueous phases. Consequently, the surface potential of the left side of the membrane changes during the reaction cycle. When the membrane is illuminated with short flashes, this change of the surface potential of one interface can be measured.

The discussion in this communication will be restricted to flash experiments, since the concept of "chemical capacitance" has been specifically derived from this type of experiment. The corresponding measurements have been performed with a special type of electronic current amplifier, designated as "tunable voltage clamp" or "TVC-method" (Hong and Mauzerall, 1976). To analyze the experimental data, the authors have carried out a complete circuit analysis and have taken into account the electrode access impedance as well as the tuned amplifier impedance. For a typical experiment the error voltage, i.e., the voltage drop across the effective access impedance, was 1.2 mV, and the computed photovoltage under zero current was 1.6 mV (Hong and Mauzerall, 1976). Thus, the method does not perfectly voltage clamp the membrane since the intentionally slowed response of the clamp will not maintain the voltage constant at all times.

THE EQUIVALENT CIRCUITS

Fig. 1 shows two equivalent circuits as proposed by Hong (1976). These are the equivalent circuits for the so-called hybrid model and for the microscopic model, respectively. Both circuits consist of the usual parallel combination of the membrane resistance R_m and the membrane capacitance C_m. The components for the photochemical reaction are placed in parallel. The reactive part is represented by a photo-emf $E_p(t)$ connected by a series resistance R_p to another parallel combination of a resistance R_s and a capacitance C_p (hybrid model) or C_p' (microscopic model). The microscopic model contains the additional capacitance C_d parallel to the photo-emf (C_d = capacitance of the diffuse ionic double layer). The capacitance C_p is called "novel chemical capacitance" (Hong and Mauzerall, 1974).

From a general point of view, it is puzzling that ". . . the photo-emf is connected in parallel with the membrane capacitance C_m . . ." (Hong and Mauzerall, 1976) and not in series, because the photochemical reaction under study is a charge transfer between an electron acceptor in the aqueous phase and an electron donor located in the polar headgroup region of the membrane. Accordingly, the electron transfer does not occur across the membrane. Thinking in molecular terms one could prefer the following architecture: electrolyte/ionic double layer of the left interface/bilayer membrane/ionic double layer of the right interface/electrolyte (Fig. 2 *a*). The arrangement of the corresponding equivalent capacitances in an

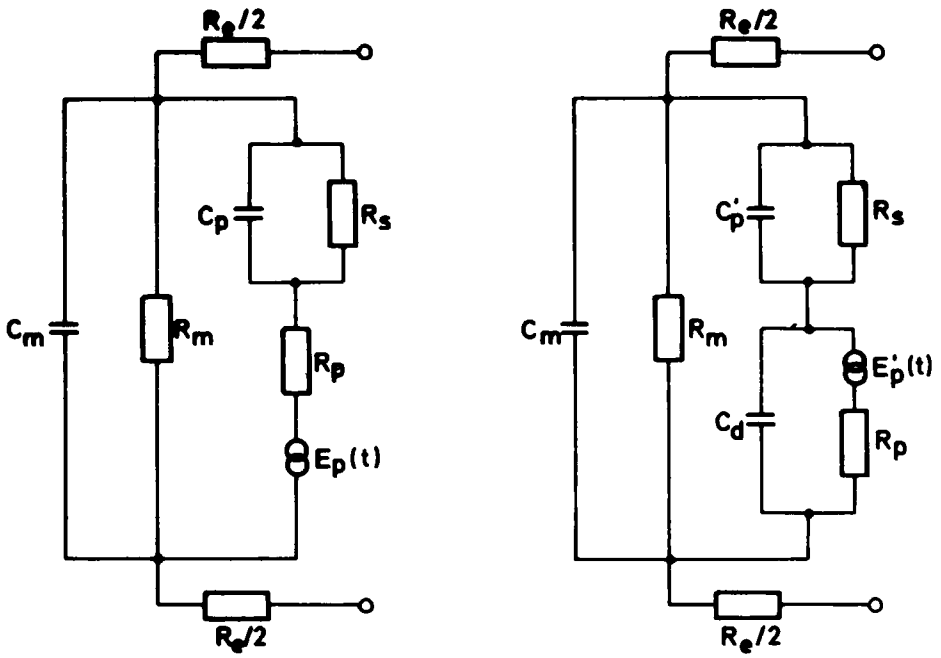

FIGURE 1 Equivalent circuits according to Hong (1976). (*a*) R_m, membrane resistance; C_m, membrane capacitance; $E_p(t)$, photo-emf of the interface reaction; C_p, chemical capacitance; R_p, chemical resistance or interfacial resistance; R_s, transmembrane resistance; R_e, effective access resistance. Additional symbols used in *b*: C_d, capacitance of the left-side ionic double layer; C_p', a combination of the membrane geometric capacitance with the right-side double layer capacitance according to Eq. 2.

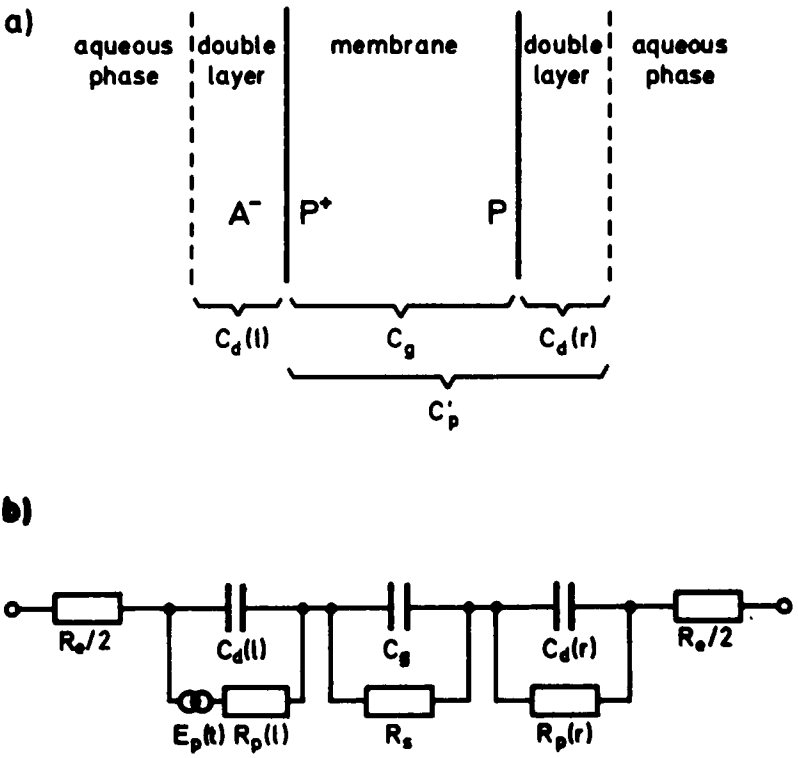

FIGURE 2 (*a*) Schematic diagram of the pigmented lipid bilayer membrane, illustrating the geometric capacitance of the bilayer, C_g, and the two diffuse ionic double layer capacitances $C_d(l)$ and $C_d(r)$ at the left and right interface, respectively. (*b*) Equivalent circuit derived from Fig. 2 *a* and composed of elements of Fig. 1 assuming that the entire membrane is illuminated. In addition to the capacitances of *a*, the circuit includes a photo-emf, $E_p(t)$, the interfacial resistances $R_p(l)$ and $R_p(r)$, and the transmembrane resistance, R_s, as well as the electrode resistance, R_e.

equivalent circuit which includes the photo-emf as well as resistors for the ionic conductances is shown in Fig. 2 *b*. The apparent contradiction between the equivalent circuits of Hong and this straightforward picture will be the subject of the following discussion.

One fundamental problem, inherent in a description of an experiment by an equivalent circuit, is the lack of uniqueness. Even if an irreducible model is found, it is often difficult to assign molecular reality to capacitors and resistors. Great care must be taken to cross-check the consistency between the experiment and the model. In the present case, a reasonable test would be to measure the photocurrent and the photovoltage and compare the results with the theoretical calculations based on the circuits.

There is general agreement that photocurrent measurements and photovoltage measurements provide equivalent information concerning the membrane photoreaction. Hong states: "Since the current source description and the voltage source description are interconvertible and equivalent to each other, one need to consider only one of them" (Hong, 1976). Consequently, Hong has measured only one independent quantity, the photocurrent. The photovoltage, however, is computed from the photocurrent using equations derived from the equivalent circuits (Fig. 6 in Hong and Mauzerall, 1976; or Fig. 18 in Hong, 1976).

Furthermore, Hong discriminates between a measured photovoltage and the photo-emf $E_p(t)$ of the photochemical reaction. Thus, there exists a further *a priori* unknown quantity. Hence, the system is insufficiently determinate. For this reason the "chemical capacitance" derived in this way may be questioned.

THE MEANING OF "CHEMICAL CAPACITANCE"

Taking a molecular picture as his guide, Hong (1976) outlined "... a microscopic model, from which the macroscopic characteristics of the hybrid model will be derived" (see also Fig. 1 *b* and Fig. 2 *a* and *b*). In that study Hong described the microscopic model as the left-side double layer capacitance $C_d(l)$, the geometric capacitance of the bilayer membrane C_g, and the right-side double layer capacitance $C_d(r)$ joined together in series. The site of the photochemical reaction, i.e., the photo-emf "... is in parallel with the double layer capacitance of the adjacent interface and in series with the geometric capacitance and the double layer capacitance of the other interface" (Hong, 1976). For convenience, C_g and $C_d(r)$ were combined to form a single capacitance (Hong, 1976):

$$\frac{1}{C'_p} = \frac{1}{C_g} + \frac{1}{C_d(r)}. \tag{2}$$

To correlate the hybrid model (empirically derived from the circuit analysis) with the microscopic model (derived from a reasonable molecular picture), Hong compared the mathematical treatments of both. He finds the identification:

$$C_p = C'_p + C_d(l). \tag{3}$$

This equation is essential since it relates the abstract "chemical capacitance" with well known physico-chemical capacitances. Eq. 3 defines the "chemical capacitance" as a parallel combination of C'_p and $C_d(l)$. Since both models are formulated independently of each other, Eq. 3, strictly speaking, must be considered as an equation that describes only a relation between two models and not a relation in one model that describes the experiments.

Quite apart from this formal argument, such a parallel combination is unrealistic in molecular terms: it would mean that the "chemical capacitance" C_p is a parallel combination of the left-side double layer capacitance and the series combination of the geometric membrane capacitance and the right-side double layer capacitance. In other words, the photoreaction would be in parallel to the membrane contradicting the microscopic model, which assumes that the photoreaction occurs in front of the membrane, i.e., in series.

This contradiction and the previous argument lead one to suspect that the "chemical capacitance" is not what it is made out to be by Hong. The contradiction is more obvious when we make a quantitative estimation of the capacitances involved. Let us assume a specific lipid bilayer capacitance of $C_g = 1\ \mu F \cdot cm^{-2}$ and an ionic strength of 1 M in the aqueous phase on both sides of the membrane. This is the ionic strength used in the experiments of Hong and Mauzerall (1974). Then the capacitances of the diffuse ion double layers $C_d(l)$ and $C_d(r)$ are of the order of $100\ \mu F \cdot cm^{-2}$ according to the Gouy-Chapman theory (e.g., Hiemenz, 1977). With these two values, Eq. 2 yields $C'_p = 0.99\ \mu F \cdot cm^{-2}$ and then Eq. 3 yields $C_p = (0.99 + 100)\ \mu F \cdot cm^{-2} \approx 100\ \mu F \cdot cm^{-2}$. Hence, the calculated "chemical capacitance" is approximately equal to the double layer capacitance. By contrast, the experimentally determined

value (normalized to 1 cm^2) of the "chemical capacitance" was $C_p = 0.16\ \mu F \cdot cm^{-2}$ (Hong and Mauzerall, 1974).

This striking discrepancy of almost three orders of magnitude has not been discussed by Hong. However, it was mentioned by Mauzerall (1979). In this study Mauzerall infers a reduction of the effective capacitance of the interfacial region from the discrete charge effect (Andersen et al., 1978) and the finite size of the ions and the polar groups at the interface (compare also Stark and Gisin, 1979). However, this would mean that the "chemical capacitance" is related to boundary layers, contradicting the previous straightforward identification of the "chemical capacitance" with the well-defined Gouy-Chapman double layer capacitance.

It appears as if Hong is talking about two different "chemical capacitances," one derived from an equivalent circuit and the other representing the diffuse ion double layer. In the next section we will look for an explanation.

EXPLANATION OF THE DISCREPANCIES

According to Hong and Mauzerall, the laser flash illuminates only ~20% of the bilayer membrane area. This experimental peculiarity, however, has not been incorporated into the circuit analysis: "... no attempt has been made to take into account the effect of focused illumination ..." (Hong and Mauzerall, 1976, p. 1320; Hong, 1976, p. 172) and "The above model is oversimplified, because it neglects ... the fact that we illuminate specifically only a fraction of the biomolecular region of the total membrane" (Hong and Mauzerall, 1974, p. 1565).

When the bilayer membrane is partially illuminated, it can no longer be regarded as one unit, but rather has to be divided into a photoelectrical active part and a parallel connected passive part. This, exactly, is described by the equivalent circuits in Fig. 1: the source of the photo-emf is AC-coupled to the opposite electrolyte solution by a capacitance which may represent that fraction of the total membrane area that is excited. This subcapacitance can now be considered as a "chemical capacitance C_p." Its magnitude can be calculated from the specific membrane capacitance ($\approx 1\ \mu F \cdot cm^{-2}$) and the illuminated area. In this picture, the only meaningful way of connecting the inactive membrane fraction to the active one would be the parallel connection similar to the equivalent circuits of Fig. 1. Hence, these circuits describe the experimental detail of partial illumination.

Of course, in this picture the inactive fraction of the membrane capacitance would be $(C_m - C_p)$, whereas the inactive fraction in the equivalent circuits in Fig. 1 is C_m. According to the numerical values published by Hong and Mauzerall (1974), C_p is 16% of C_m. (The difference between C_m and $[C_m - C_p]$ was probably too small to have been noticed.)

Following this line of reasoning one can calculate C_p from the percentage of the illuminated membrane area. According to Hong and Mauzerall (1974), the laser beam was focused on 19% of the bilayer area. Since the total bilayer had a capacitance of 8.2 nF, the photochemically excited fraction corresponds to 1.5 nF. In the same paper, the "chemical capacitance" was measured to be $C_p = 1.3$ nF. Both values compare well in view of the fact that a laser beam has a diffuse periphery, so that its diameter is not well-defined. We see that in this interpretation the theoretical and the experimental value of the "chemical capacitance"

coincide, whereas in Hong's interpretation a discrepancy of almost three orders of magnitude remains to be explained (Mauzerall, 1979).

Direct experimental evidence for this interpretation is given by Hong himself (1976) when he discusses a scanning experiment. In this experiment the laser beam (one-sixth of the membrane diameter) was moved across the pigmented bilayer membrane to reveal the photoelectrical activity of the thin bimolecular region and the thick annulus region (Plateau-Gibbs border). The experiment showed that ". . . the chemical capacitance is much larger at the thin bilayer region than at the thick annular region" (Hong, 1976; footnote on p. 182). Such a finding agrees well with a model where the "chemical capacitance" reflects the membrane AC-coupling capacitance of the photo-emf to the electronic amplifier, since a thick membrane has a smaller capacitance than a thin membrane.

Although this alternative interpretation of the "chemical capacitance" is consistent with the numerical value determined by Hong, it is not compatible with Hong's microscopic interpretation of C_ρ in terms of the Gouy-Chapman theory. The discrepancy is due to the inconsistency in Hong's analysis: in the microscopic picture the membrane area is tacitly assumed to be homogeneously excited, whereas in the equivalent circuits a photochemically active part is distinguished from an inactive one.

CURRENT-VOLTAGE RELATION

Photoelectric signals from capacitative systems can be measured either as a photocurrent or as a photovoltage. To measure a current, the impedance of a current amplifier must be much smaller than the source impedance, while to measure a voltage, the source impedance must be much smaller than the impedance of a voltage amplifier (equal to impedance matching conditions). All three impedances decrease with increasing frequency in the following order: source impedance, current amplifier impedance, and voltage amplifier impedance. To fulfill the impedance matching condition voltage amplifiers are therefore more appropriate than current amplifiers when measuring short electrical events from capacitative objects. It has been shown that a proper impedance matching with voltage amplifiers can be achieved at least up to 100 MHz (Huebner, 1979; Trissl, 1980; Trissl and Gräber, 1980). In comparison, the official limiting frequency of the TVC-method is ~2 MHz, as derived from the rise-time of 150 ns (Hong, 1976) and using the formula

$$f_{3\,\mathrm{db}} = \frac{0.35}{\tau_{10\text{-}90\%}}. \tag{4}$$

As discussed elsewhere in more detail (Trissl, 1980), at a given frequency the voltage clamp mode causes larger currents to flow in the measuring circuit than the current clamp mode does. A larger current means a larger error voltage and this results in a lower limiting frequency of the voltage clamp method as compared with the current clamp method. The faster an instantaneous electrical event in a capacitative system is measured, the more the initial current will increase and the more the voltage clamp mode will approach the current clamp mode, as is the case for the TVC-method. However, the TVC-method takes this effect into account and therefore most likely reveals correct kinetic data of the photochemical reaction.

The relation between a current and a voltage registration in the kilohertz range under sufficiently ideal conditions has been described recently (Trissl, 1979, 1980). In these articles, it was shown by appropriate test experiments that, in accordance with an equivalent circuit, the current is the first time derivative of the voltage, provided that the membrane is illuminated homogeneously and the molecular reaction at the membrane is independent of the external measuring conditions. The latter stipulation is not trivial and must therefore be examined for every individual system studied. It may be noted that Hong has not reported an experimental current-voltage relation in the porphyrin-containing bilayer membranes under flash excitation.

CONCLUDING REMARKS

Any partial illumination of a photoelectrical active membrane causes an inhomogeneity: the membrane is split into an active and an inactive region. Depending on the measuring method, current clamp or voltage clamp, intrinsic charge redistribution processes may lead to additional relaxations which would not be present when the membrane was fully illuminated. In the ideal voltage clamp mode this effect is expected to be negligible, since the potential of the membrane in the illuminated and unilluminated region is the same, whereas in the current clamp mode this effect may be significant, since the membrane potentials of the illuminated and unilluminated region differ and the measured potential would be some complex sum of the two. As mentioned before, the TVC-method is classified between a voltage clamp and a current clamp method. Therefore, it is difficult to estimate the influence of this effect on the measured reaction time constants.

It is worth bearing in mind that until now no other experimental system has been reported where the "chemical capacitance" could be derived. This applies especially for an investigation on the photoelectrical activity of thin bacteriorhodopsin layers (Hong and Montal, 1979), where the authors neither quoted a numerical value for C_p nor discussed the "chemical capacitance" at all, although this experimental system with simple planar geometry would offer the possibility of an independent proof of the "existence of the chemical capacitance." In addition, the "chemical capacitance" was also not required to interpret the experimental data obtained from several other photoelectrically active membrane systems (Tien, 1972; Ullrich and Kuhn, 1972; Schadt, 1973; Berns, 1976; Bamberg et al., 1979; Duchek and Huebner, 1979).

In particular, the author's own measurements of the photosynthetic charge separation in interfacial layers of thylakoids do not indicate an additional capacitance other than those generally used for analysis (Trissl and Gräber, 1980). In this special case, the knowledge that the photosynthetic charge separation takes place in picoseconds and lasts up to milliseconds (Witt, 1979) could be used to verify the consistency between experiment and circuit analysis.

In conclusion, the photochemical experiments and the corresponding circuit analysis in the work of Hong and Mauzerall are formally consistent with each other. The experimental, as well as kinetic, data reported are not called in question here. However, the "chemical capacitance" deduced is questioned for the following reasons: (*i*) The system analysis is insufficiently determinate. (*ii*) The measured chemical capacitance is smaller by a factor of almost 10^3 than that predicted by the theory. (*iii*) The fact that only part of the membrane area is illuminated has not been considered in the analysis. In the present communication a

quite different interpretation of the equivalent circuits is suggested in which the "chemical capacitance" takes account of partial illumination of the membrane. If this interpretation were correct the "concept of chemical capacitance" lacks general significance.

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