

# Simple and direct interpretation of phase angles or derivation degrees in term of energy conservation vs. dissipation with Formal Graphs

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**Abstract** With the help of a new theory using the notion of path in a graph, a physical interpretation and meaning can be given to electroanalytical measurements, without recourse to mathematical treatments. The frequency dependence of impedances measured by ac techniques, or the scan rate dependence of current vs. potential characterizations in large signal techniques (cyclic voltammetry), can be interpreted through this approach as a determination of the proportion of conserved energy vs. total energy involved in a mechanism. This total energy includes the energy which is lost by dissipation, i.e., converted into heat. This new way of thinking sheds an interesting light on the difference between normal and anomalous or fractal diffusion and provides to the analyst a simple and immediate tool for interpreting experimental data.

**Keywords** Graph · Impedance · Voltammetry · Exponent · Fractal · Anomalous diffusion

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## Symbol list

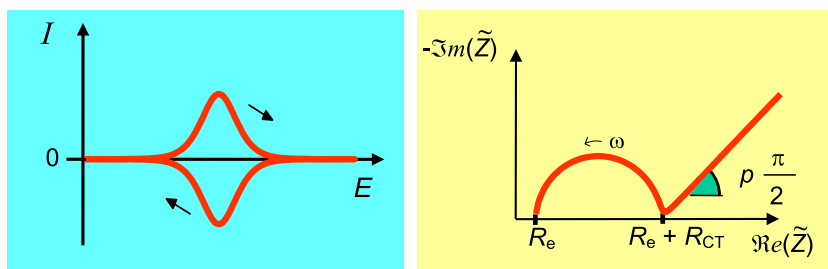
### Roman letters

A	Initial species of the reaction
A*	Initial species of the reaction in the bulk or in its initial state
A°	Initial species of the reaction on the charge transfer site
A	Area ( <i>vector</i> ) [m <sup>2</sup> ]
$\hat{A}$	Area ( <i>operator</i> ) [m <sup>2</sup> ]
B	Product species of the reaction
B*	Product species of the reaction in the bulk or in its initial state
B°	Product species of the reaction on the charge transfer site
C	Differential electric capacitance [F]
$\hat{C}$	Integral electric capacitance ( <i>operator</i> ) [F]
$\hat{C}_n$	Integral physical chemical capacitance ( <i>operator</i> ) [mol <sup>2</sup> J <sup>-1</sup> ]
$\hat{C}_q$	Integral generalized capacitance ( <i>operator</i> ) [q <sup>2</sup> J <sup>-1</sup> ] <sup>1</sup>
c	Volumic concentration of substance [mol m <sup>-3</sup> ]
c*	Bulk or initial volumic concentration of substance [mol m <sup>-3</sup> ]
$c_A^0$	Volumic concentration of species A on the charge transfer site [mol m <sup>-3</sup> ]
$c_B^0$	Volumic concentration of species B on the charge transfer site [mol m <sup>-3</sup> ]
D	Diffusivity (diffusion coefficient) [m <sup>2</sup> s <sup>-1</sup> ]
d	Differential operator
E	Electrode potential [V]
E <sub>i</sub>	Initial value of the electrode potential [V]
F	Faraday constant [≈9.64853 × 10 <sup>4</sup> C mol <sup>-1</sup> ]
e <sup>-</sup>	Electron

<sup>1</sup> q stands for the unit of the basic quantity (e.g., mol, C, m, m<sup>3</sup>, etc.) that defines the energy variety.

$e_q$	Effort (generalized potential) [J q <sup>-1</sup> ] <sup>1</sup>	$\hat{Y}_n$	Integral physical chemical admittance (operator) [mol <sup>2</sup> J <sup>-1</sup> s <sup>-1</sup> ]
$f_q$	Flow (generalized current) [q s <sup>-1</sup> ] <sup>1</sup>	$Z$	Differential electric impedance [S]
$\hat{G}$	Electric conductance [S]	$\hat{Z}$	Integral electric impedance (operator) [ $\Omega$ ]
$\hat{\hat{G}}$	Integral electric conductance (operator) [S]	$\tilde{Z}$	Fourier transform of the integral electric impedance [ $\Omega$ ]
$\hat{G}_n$	Integral physical chemical conductance (operator) [mol <sup>2</sup> J <sup>-1</sup> s <sup>-1</sup> ]	$z$	Charge number of an ion [-]
$\hat{\hat{G}}_q$	Integral generalized conductance (operator) [q <sup>2</sup> J <sup>-1</sup> s <sup>-1</sup> ] <sup>1</sup>	<b>Greek letters</b>	
$I$	Electric current [A]	$\Phi_B$	Induction flux [Wb]
$\tilde{I}$	Fourier transform of the electric current [A]	$\Gamma$	Euler or Gamma function [-]
$I_{v0}$	Scaling electric current [A]	$\lambda$	Integration variable
$\tilde{J}$	Substance flow (mass flux) ( <i>I Fraktur</i> ) [mol s <sup>-1</sup> ]	$\mu$	Chemical potential [J mol <sup>-1</sup> ]
$i$	Imaginary number ( $i^2 = -1$ )	$\mu^\theta$	Reference chemical potential [J mol <sup>-1</sup> ]
$\mathbf{J}$	Substance flow density (mass flux density) ( <i>vector</i> ) [mol m <sup>-2</sup> s <sup>-1</sup> ]	$\bar{\mu}$	Electrochemical potential [J mol <sup>-1</sup> ]
$k_A$	Forward heterogeneous rate constant ( <i>vector</i> ) [m s <sup>-1</sup> ]	$\mu_\nu$	Translated chemical potential from electrodynamics [J mol <sup>-1</sup> ]
$k_B$	Backward heterogeneous rate constant ( <i>vector</i> ) [m s <sup>-1</sup> ]	$\nu$	Frequency [Hz]
$k_{CT}^0$	Intrinsic heterogeneous rate constant ( <i>vector</i> ) [m s <sup>-1</sup> ]	$\pi$	Archimedes constant [ $\approx 3.14159$ ]
$\hat{L}$	Electric inductance [H]	$\tau$	Relaxation or characteristic time [s]
$\hat{\hat{L}}$	Integral electric inductance (operator) [H]	$\tau_{Cq}$	Capacitive time constant [s]
$\hat{\hat{L}}_q$	Integral generalized inductance (operator) [J q <sup>-2</sup> s <sup>2</sup> ] <sup>1</sup>	$\tau_{Lq}$	Inductive time constant [s]
$\ell$	Displacement, characteristic distance, thickness ( <i>vector</i> ) [m]	$\omega$	Pulsation or angular velocity [rad s <sup>-1</sup> ]
$M$	Inertial mass [kg]	<b>Introduction</b>	
$\hat{m}$	Mass transfer rate ( <i>operator</i> ) [m s <sup>-1</sup> ]	The two most important and widely used techniques among electroanalytical techniques are cyclic voltammetry and impedancemetry. In Fig. 1 are shown the plots that are characteristic of a simple charge transfer (E mechanism) according to these two techniques.	
$n$	Substance amount [mol]	The voltammogram results from the imposition of a potential sweep at a fixed scan rate $\nu$ . The usual practice is to perform a forward and backward scan (cyclic voltammetry); however, a simple forward scan is sufficient for obtaining the necessary information required in this study (linear scan voltammetry). The complex impedance diagram is the result of several measures made at various frequencies $\nu$ or pulsations $\omega$ (impedance spectroscopy), so the continuous curve in Fig. 1 is plotted by joining consecutive points. On the Nyquist plot of the complex impedance is evidenced the straight line of the low-frequency response that appears when electroactive species are transported by mass transfer between the electrode (i.e., the site of electron exchange) and the bulk (far from the site). The angle featuring the slope of this straight line is a key parameter for determining the mass transfer process. It ranges from 0 in case of stationary transport (convection) to 1 in case of absence of transport (ultrathin-layer cell or immobilized substance). The peculiar value $\pi/4$ is observed when normal transient diffusion ensures the mass transfer and other values are	
$n^\theta$	Reference substance amount [=1 mol]		
$n_e$	Stoichiometric number of electrons [-]		
$\hat{O}$	Any operator		
$\rho$	Degree of derivation or mass transfer mode [-]		
$\rho_q$	Impulse (generalized quantity of movement) [J q <sup>-1</sup> s] <sup>1</sup>		
$Q$	Electric charge [C]		
$q$	Basic quantity [q] <sup>1</sup>		
$R$	Gas constant [ $\approx 8.3144$ J mol <sup>-1</sup> K <sup>-1</sup> ]		
$\hat{R}$	Electric resistance [S]		
$\hat{\hat{R}}$	Integral electric resistance (operator) [S]		
$\hat{\hat{R}}_q$	Integral generalized resistance (operator) [Js q <sup>-2</sup> ] <sup>1</sup>		
$\mathbf{r}$	Space vector [m]		
$s$	Sink of substance [mol s <sup>-1</sup> m <sup>-3</sup> ]		
$T$	Temperature [K]		
$t$	Time [s]		
$\mathbf{u}$	Convective rate ( <i>vector</i> ) [m s <sup>-1</sup> ]		
$V$	Electric potential [V]		
$\hat{V}$	Volume [m <sup>3</sup> ]		
$\tilde{V}$	Fourier transform of the electric potential [V]		
$\nu$	Sweep rate [V s <sup>-1</sup> ]		
$\nu_0$	Scaling sweep rate [V s <sup>-1</sup> ]		
$\times$	Composition of operators by commutative multiplication (in a Formal Graph)		
$Y$	Differential electric admittance [S]		
$\hat{Y}$	Integral electric admittance (operator) [S]		
$\tilde{Y}$	Fourier transform of the integral electric admittance [S]		

**Fig. 1** Cyclic voltammetry plot (left) and Nyquist plot of the complex impedance (right) of an E mechanism

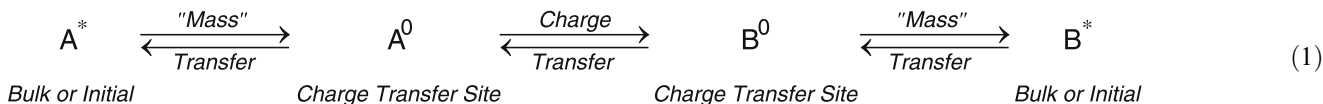


observed in case of anomalous diffusion (due to a fractal interface or to other reasons).

A cyclic voltammetry plot does not evidence directly the mass transfer behavior as in the case of impedancemetry (unless when one trusts the voltammogram shape). For obtaining equivalent information to the one given by impedancemetry, repetition of the measure at various scan rates must be done in order to determine the dependence of the current upon the scan rate. The reason comes from the operating modes that differ between the two techniques: In cyclic voltammetry, the frequency (i.e., the scan rate) is fixed and the electrode potential is varied, while the reverse is done in impedancemetry. For comparing the two techniques, a brief discussion on the model that can be used is required.

The E mechanism

The simplest electrochemical reaction  $A - n_e e^- \rightarrow B$  is classically decomposed into a sequence of more elementary steps, inserting one charge transfer (exchanging  $n_e$  electrons) step between two mass transfer steps. A first mass transfer brings the electroactive species (notated  $A^*$  for indicating a localization in the bulk) to the site of the charge transfer, and then electron exchange occurs between the species  $A^\circ$  and the site (electrode) giving a species  $B^\circ$  that is transported away. This usual mechanism, which belongs to the category of faradaic processes (in contradistinction with double-layer charging or electrolyte conduction), is written as



This scheme is valid for all cases of mass transfer, even in the case of immobilized substances (or ultrathin-layer cell). In most cases indeed, mass transfer is a transport of substance between the bulk and the site (electrode), ensured by diffusion, convection, or migration. However, in peculiar situations, no transport actually occurs because all active species are immobilized onto an electrode and electrons are moving between them and the electronic conductor making up the electrode. In that case,  $A^*$  stands for the initial substance and  $B^*$  is the final product of the reaction (they are not chemically distinct from  $A$  and  $B$ , but their amount correspond to the quantities having not yet reacted and having reacted, respectively). The mass transfer steps are in fact evolution steps without displacement, and only the sites are moving from one electroactive species to the other. They must remain elemental steps without involving other processes, such as for instance gas evolution from immobilized substance, which is a more complex mechanism. As example of elemental step, ultrathin-layer cells involve only evolution when they are sufficiently thin for neglecting the movement of the species

in comparison with the displacement of sites. Increasing the thickness of the cell makes the transport progressively dominating the evolution, so a continuum between pure evolution (no transport) and pure transport (all species are moving) can be observed by varying the cell thickness. This gives consistence to the proposal made earlier by the author to enlarge the notion of mass transfer for including the ultrathin-layer case into it [1, 2].

With this extension of the notion of mass transfer, the three-step mechanism described above models all cases of transport and absence of transport that may be encountered in practical electroanalytical conditions. It is commonly admitted among electrochemists using ac modulation techniques or impedancemetry that the above sequence of reaction steps is translated into a sum of individual impedances, one for each step [3]. This sum corresponds to the total impedance of the reaction that is measured by the mentioned techniques. However, this reasoning is not restricted to the case of small amplitude periodic signals and can be generalized to any amplitude and shape of signal, by replacing the complex impedance by a more

general notion which is the integral impedance  $\widehat{Z}$ , notated with a hat because it is an operator and neither a complex quantity nor a real scalar. In terms of integral impedances, the sum featuring the A  $\rightarrow$  B mechanism is written

$$\widehat{Z} = \widehat{Z}_A + \widehat{Z}_{CT} + \widehat{Z}_B \quad (2)$$

in which impedances subscribed with a species letter represent the respective mass transfer impedances whereas the subscript CT refers to the charge transfer step.

The composition of impedances given above is in fact a simplified model because other processes influencing the electrical response occur in an electrochemical cell, such as the electrolyte resistance (ohmic drop) or the double-layer capacitance or space charges in a semiconductor. It will be assumed in the followings that these non-faradaic processes can be neglected by choosing a range of scan rates or frequencies in which the faradaic process is predominant.

### Integral and complex admittances

In electrodynamics, the impedance is algebraically written as relating the current  $I$  to the potential difference  $V$  that exists across the component under measure, these variables being Fourier-transformed (notated with a tilde) in case of complex impedance.

$$\text{(Integral)Impedance } V = \widehat{Z}I \quad \text{Complex Impedance } \tilde{V} = \tilde{Z}\tilde{I} \quad (3)$$

These relationships can be inverted by using the reciprocal of the impedance called admittance and notated  $\widehat{Y}$ ,

$$\text{(Integral)Admittance } I = \widehat{Y}V \quad \text{Complex Admittance } \tilde{I} = \tilde{Y}\tilde{V} \quad (4)$$

The Fourier transform makes the correspondence between integral and complex quantities

$$\widehat{Z} \xrightarrow{\text{Fourier}} \tilde{Z} \quad \widehat{Y} \xrightarrow{\text{Fourier}} \tilde{Y} \quad (5)$$

It can be remarked that the plot shown in Fig. 1 of a cyclic voltammogram represents the integral admittance since the measured current is plotted against the imposed potential. In mathematical terms, the curve represents the trace of the admittance operator. For this reason, the discussion will be made exclusively in term of admittance in mentioning that this is not a difficulty in impedancemetry since the choice between impedance or admittance representation is purely a question of tradition among electrochemists using this technique.

In electrodynamics, the concept of admittance/impedance is used in the same manner as the unknown variable  $x$  in algebra for representing a quantity without knowing its value. Thus, an admittance may model several basic

components, such as capacitor, resistor, and inductor in adapting the expression of the operator to their electrical behavior. The general expression for the admittance of all these components is algebraically written as proportional to the time derivation raised to a power  $\rho$ ,

$$\text{(Integral)Admittance } \widehat{Y} \propto \frac{d^\rho}{dt^\rho} \quad \text{Complex Admittance } \tilde{Y} \propto (i\omega)^\rho \quad (6)$$

The expression of the complex admittance stems from the following rule used for obtaining the Fourier transform of the time derivation:

$$\frac{d}{dt} \xrightarrow{\text{Fourier}} i\omega \quad (7)$$

which says that the result is the product of the imaginary number with the pulsation  $\omega$ .

The value of the exponent  $\rho$  depends on the nature of the component: +1 for a capacitor (full time derivation), 0 for a resistor (no time derivation), and -1 for an inductor, with the convention of notating the time integration (between 0 and  $t$ ) as the reciprocal of the time derivation.

$$\frac{d^{-1}}{dt^{-1}} f(t) = \int_0^t f(t) dt \quad (8)$$

### Dependence upon scan rate or frequency

Before detailing this point, the discussion is focused on the way this exponent  $\rho$  can be determined by cyclic voltammetry when the admittance of the E mechanism is effectively proportional to the time derivation raised to a constant power. The shape of the electrode potential variation for the forward scan is given by the linear relation

$$E = E_i + v t \quad (9)$$

In this relation,  $E_i$  is the initial potential and  $v$  is the scan rate, which is a constant chosen by the operator of the technique. This constancy allows writing the time derivation under the form of a derivation with respect to the potential

$$\frac{d}{dt} = v \frac{d}{dE} \quad (10)$$

Raised to the power  $\rho$ , this equivalence provides the general expression of the admittance

$$\text{Admittance } \widehat{Y} \propto v^\rho \frac{d^\rho}{dE^\rho} \quad (11)$$

Since the current results from applying this operator to the potential, it can be expressed under the form of proportionality to the scan rate raised to the power  $\rho$

$$I = I_{V_0} \left( \frac{v}{v_0} \right)^\rho \quad (12)$$

Linearization of this relation is made by plotting the logarithms of the two variables, as shown in Fig. 2 left.

The comparison between the two plots in Fig. 2 shows that both techniques produce equivalent information regarding the behavior of the admittance, which describes the relationship between potential and current. It must be stressed that the observation of a straight line relies on the predominance of kinetic steps that obey to the proportionality to the time derivation with the same derivation degree, as given in Eq. 6, in including the case of time invariance ( $\rho=0$ ). When several steps dominate the mechanism kinetics, with different dependence upon the time derivation, a non-linear behavior is observed for some scan rates or frequencies, as for instance in the complex impedance shown in Fig. 1 where the semi-circle expresses the influence of non-faradaic processes.

Electric components

The classical analysis of the complex admittance or impedance in electrodynamics consists in identifying the experimental response with the typical behavior of known components. An electrical circuit composed of several components can generally be deduced from experimental responses in case of contributions of different behaviors. This method can be extended outside ac techniques by using integral admittances without difficulty because all component properties, capacitance, conductance, and inductance are scalars in classical electrodynamics. In Table 1 are listed the main components that are used for interpreting experimental responses.

In addition to the three basic components is the constant phase element (CPE) which is defined as being modeled by an admittance proportional to the time derivation raised to a non-integer exponent  $\rho$ . In the expressions of this admittance is used a characteristic time  $\tau$  that plays the role of scaling factor for the time.

It may be useful to recall how a fractional integral can be evaluated with the classical tools of mathematical analysis. The Riemann–Liouville  $\rho$ -integral, originally established for finding how to reduce a multiple integration of order  $\rho$  to a single one, provides the tool by extending the order of integration to non-integer values. This  $\rho$ -integral is a convolution with a Green function, defined as the integra-

**Table 1** Correspondence between components of an equivalent electric circuit and integral or complex admittances in the linear approximation

Components	(Integral) admittance	Complex admittance
Inductor ( $\rho=-1$ )	$\hat{Y} = L^{-1} \frac{d^{-1}}{dt^{-1}}$	$\tilde{Y} = (i\omega L)^{-1}$
Conductor ( $\rho=0$ )	$\hat{Y} \stackrel{\text{lin}}{=} G = R^{-1}$	$\tilde{Y} \stackrel{\text{lin}}{=} G$
Capacitor ( $\rho=1$ )	$\hat{Y} \stackrel{\text{lin}}{=} \frac{d}{dt} C$	$\tilde{Y} \stackrel{\text{lin}}{=} i\omega C$
CPE ( $-1 < \rho < 1$ )	$\hat{Y} \stackrel{\text{lin}}{=} G \tau^\rho \frac{d^\rho}{dt^\rho}$	$\tilde{Y} \stackrel{\text{lin}}{=} G(i\omega\tau)^\rho$

tion variable raised to the power  $\rho-1$  divided by the Gamma, or Euler, function of  $\rho$  [4].

$$\frac{d^{-\rho}}{dt^{-\rho}} f(t) = \frac{t^{\rho-1}}{\Gamma(\rho)} \times f(t) = \frac{1}{\Gamma(\rho)} \times \int_0^t \frac{f(\lambda)}{(t-\lambda)^{1-\rho}} d\lambda (\rho > 0) \tag{13}$$

This approach works only for integer or non-integer integrations, and for working in the opposite way, the rule of composition of operators raised at various powers allows evaluation of a non-integer derivation from the previous integration

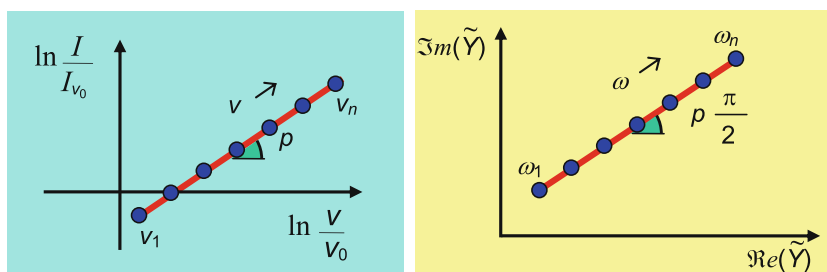
$$\frac{d^\rho}{dt^\rho} = \frac{d}{dt} \frac{d^{-(1-\rho)}}{dt^{-(1-\rho)}} \tag{14}$$

The Formal Graph approach

All the preceding discussion has been made in the frame of the classical and widely used theories in electrodynamics and in electrochemistry. A more detailed discussion could have been made on the correspondence that is classically established between electrical components and electrochemical kinetics, but this is not the scope of this paper to reproduce this known part of the electrochemical science, which can be found in many textbooks [3].

The Formal Graph theory is a graphic language that has been developed with the aim to unify the various formalisms in use through a wide range of scientific domains, from physics to chemistry in going through electrochemis-

**Fig. 2** Plot of the dependence of the logarithm of the current against the logarithm of the scan rate in cyclic voltammetry (left) and plot of the linear part of the Nyquist plot of the admittance (right). Both plots are made up of discrete points obtained at fixed scan rates and frequencies



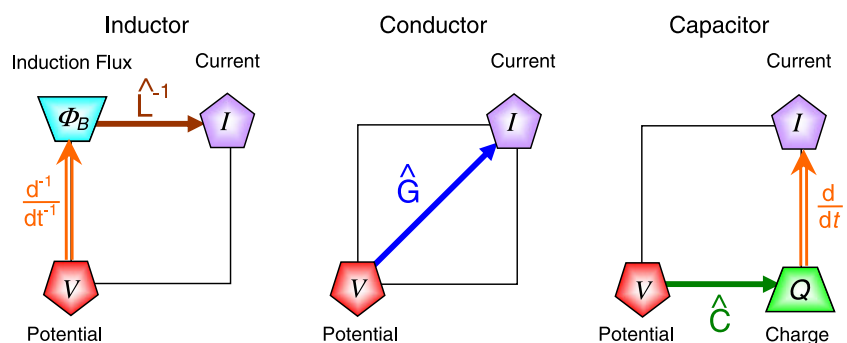
try [5, 6]. The seeding idea came from the difficulty to model complex materials such as electronic conducting polymers that are entitled with many properties relevant from electrodynamics, hydrodynamics, mechanics, capillarity (superficial energy), physical chemistry, thermics (heat), and so on. In each domain is found a different way to define or to call analog concepts (for instance, electrical capacitance and electrochemical pseudo-capacitance), and discrepancies are often considered as inherent to science. In fact, the Formal Graph approach reveals much more common concepts than it is believed, and a common background can be set up that helps to practice a transverse approach through many domains. Since the foundations of this new language can be found in several publications [5–8], we introduce abruptly in Graph 1 the translations of the three models of electric components discussed previously.

### Principle of Formal Graphs

Nodes are the four state variables in electrodynamics, charge  $Q$ , potential  $V$ , induction flux  $\Phi_B$ , and current  $I$ ; links are the space–time property of evolution (time derivation or integration) and the three system constitutive properties, capacitance  $\hat{C}$ , conductance  $\hat{G}$ , and the reciprocal of the inductance  $\hat{L}^{-1}$  (called reluctance). The important difference with the classical approach in electrodynamics is that for unifying concepts through all domains, the system constitutive properties are not considered as scalars but as operators or functions (notated with a hat).

In Graph 2 is shown the correspondence between a Formal Graph in the “normal space” and in the Fourier-transformed space (by “space” is meant here a mathematical frame in which variables are defined). In the normal space, also called “temporal space,” are found state variables and properties that are defined in the real world, as those used for the integral admittance. In the Fourier-transformed space, also called “frequency space,” are met all Fourier-transformed variables and properties that are used for the complex admittance. Note that when a property is a constant (time invariant) in the normal space, its Fourier transform is also a constant (and conversely).

**Graph 1** Three Formal Graphs modeling the basic electrical components, inductor (*left*), conductor (*center*), and capacitor (*right*)



What can be observed in Graph 2 is the strict identity of structure between the two Formal Graphs. This means that we can use the same Formal Graph structure in both mathematical spaces, normal and Fourier-transformed, and that all reasoning made in one of them, in terms of existence of links and combination of links, does not need to be repeated in the other. This simplifies the discussion, and from now, we consider only temporal Formal Graphs in knowing that extension to frequency Formal Graphs can be simply made in substituting variables and operators by their Fourier transforms.

The generalization made above consisting in using operators does not forbid retrieving a scalar featuring a linear relationship between charge and potential (as is the classical rule in electrostatics) in restricting the variation range of the variables so as to approximate the behavior to a linear asymptote. This non-conventional approach allows modeling electrochemical systems without the constraint of having to linearize electrochemical laws (Nernst, Butler–Volmer...) for establishing correspondence with electrical properties.

This generalization can be translated back into algebraic form in writing the three admittances that were given with their classical form in Table 1.

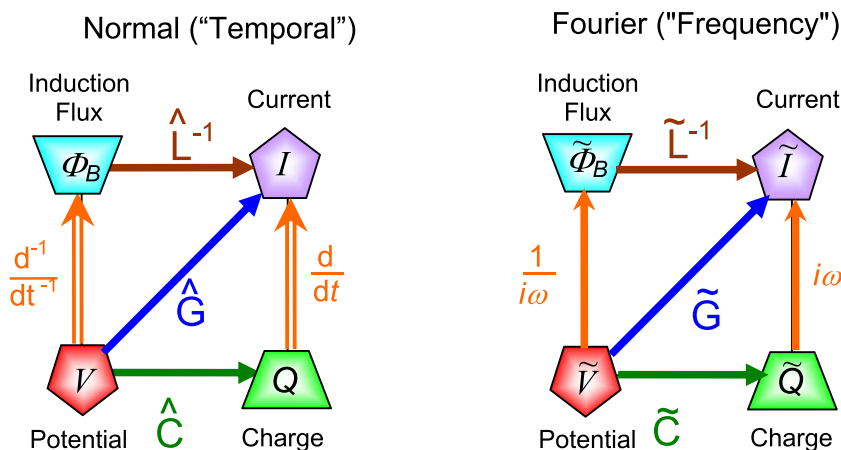
$$\hat{Y}_{\text{Inductor}} = \hat{L}^{-1} \frac{d^{-1}}{dt^{-1}} \quad \hat{Y}_{\text{Conductor}} = \hat{G} = \hat{R}^{-1} \quad \hat{Y}_{\text{Capacitor}} = \frac{d}{dt} \hat{C} \quad (15)$$

### Links in a Formal Graph

The Formal Graphs shown previously are using four different operators for linking the nodes. They are not the only ones able to link nodes in a Formal Graph, since the role of space and the way to associate different energy varieties (mechanical, physical chemical, thermal...) in a same system are not included. The following Table 2 gives a list of various elementary links with their action on energy.

The subscript  $q$  used for notating generalized constitutive properties allows attribution of the property to a given energy variety by substituting  $q$  by the characteristic state variable (called basic quantity) that identifies the variety (for example,  $\hat{C}_n$  stands for the physical chemical capaci-

**Graph 2** Generic Formal Graphs (i.e., not modeling a peculiar system) in the “normal space,” said “temporal” (left), and in the Fourier-transformed space, said “frequency space” (right)



tance, the operator linking the number of moles  $n$  to the chemical potential  $\mu$ ).

The generalized inductance  $\hat{L}_q$  is a property that allows a system to store “inductive” energy, the unified name proposed for encompassing kinetic or electromagnetic energies. When a body possesses an inertial mass  $M$  (that could be notated  $L_\ell$  because the displacement  $\ell$  is the basic quantity in mechanics), it may store some kinetic energy, and when it possesses an inductance  $L$ , electromagnetic energy can be stored. Both  $M$  and  $L$  are generalized inductances. The same principle applies to the generalized capacitance  $\hat{C}_q$  that allows a system to store another form of energy called “capacitive” in which are found heat and potential, internal, electrostatic, elastic... energies. Both inductive and capacitive energies are sub-varieties of a same energy variety. For instance kinetic and potential energies are sub-varieties of the translational mechanical energy.

The third system constitutive property is the generalized conductance  $\hat{G}_q$ , which in contradistinction with the two other properties, inductance and capacitance, cannot entitle the system to store energy but has effect to convert energy into heat. This is this property that is responsible of energy losses, called dissipation, in every process and at the origin of irreversible behaviors.

Within the category of space–time properties, the evolution link, featured by the time derivation or integration, allows conversion from capacitive energy to inductive energy and vice versa. This property, together with the

other space–time property, space distribution, is identical for all energy varieties because space and time are hosting all systems and all energy varieties.

Naturally, the state variables that are placed in the nodes must be adapted to the considered energy variety. Each node corresponds to a family of state variables that are called *basic quantity*, *effort*, *impulse*, and *flow*. These names are borrowed from the theory of network thermodynamics developed by Oster et al. [9]. For reasons of concision, the whole description of all energy varieties is not possible here, so the presentation made in Table 3 is limited to the two main varieties of interest in electrochemistry that are electrodynamics and physical chemistry.

Note that the lack of impulse in physical chemistry comes from the absence of inductive energy (analogous to kinetic or electromagnetic energy) in this variety. With these concepts, a set of four nodes representing state variables in a given energy varieties, linked by generalized system constitutive properties or space–time properties, one has a basic brick able to practically model the main laws in physics and chemistry (by eventually associating several bricks).

Energetic paths

The preceding discussion was focused on the elements of the Formal Graph language that allow word-to-word translation of the algebraic formalism used in modeling systems. However, contrary to algebra, a graph is based

**Table 2** The various operators used in a formal graph for linking nodes, sorted by category and with their physical meaning

Link category	Elementary path	Operator	Physical meaning
System constitutive properties	Inductance	$\hat{L}_q$	Energy storage
	Capacitance	$\hat{C}_q$	Energy storage
	Conductance	$\hat{G}_q$	Energy dissipation
Space–time properties	Evolution	$\frac{d}{dt}$	Energy conversion
	Space derivation	$\frac{d}{dF}$	Energy distribution/spreading (through space)
Energetic coefficients	Energy coupling	$\lambda$ (scalar) example: $zF$	Association of several energies

**Table 3** The four families of state variables and correspondence within each family between state variables belonging to electrodynamics and physical chemistry

Energy sub-variety	Electrodynamics	Physical chemistry	Generalized
Capacitive	Charge $Q$	Substance amount $n$ (mole number)	Basic quantity $q$
	Potential $V$	Chemical potential $\mu$	Effort $e_q$
Inductive	Induction flux $\Phi_B$	(not in use)	Impulse $\rho_q$
	Current $I$	Substance flow $\mathcal{J}$ (mass flux)	Flow $f_q$

on topology. It introduces the concept of path when one goes from one node to other one somewhere in the graph by taking a sequence of links (properties of graphs are described in Berge [10]). This possibility to compose several links into a path is an interesting feature that we are going to use in conjunction with the physical meaning attributed to each link for finding out physical interpretations.

When a path is not composed with conductance, the path means that conservation of energy prevails in the process, and as soon as a conductance is encountered along the path, dissipation of energy occurs. The various electric components listed in Table 1 are generalized to any energy variety and represented in the following formulas and graphs (Graphs 3, 4, 5, 6, and 7). They show the three different models that describe a same component: the algebraic formula of the admittance first, then the elementary Formal Graph and at last the Formal Graph representing paths composed with elemental links.

Translation of the general algebraic model of the CPE cannot be done with a single Formal Graph. According to the sign of the exponent  $\rho$ , one has to distinguish two CPEs, one inductive ( $-1 < \rho < 0$ ) and the other capacitive ( $0 < \rho < 1$ ). These two translations are shown in Graph 6 and 7.

**Complementing paths**

In the Formal Graph theory, the CPE is seen as a double component, working with two parallel paths, one inductive or capacitive, and the other purely conductive. However, in

the general case, the two paths are not equivalent. The importance of each path, or weight, is featured by a coefficient which is the exponent of their operator when the two paths are combined on their arrival node.

The operation made for combining the two paths is a multiplication between the results of the two operators, each one raised to the power corresponding to the weight of the path. This is illustrated in the following scheme, in which the operators are notated  $\hat{O}_1$  and  $\hat{O}_2$ . The weights  $\rho_1$  and  $\rho_2$  must comply with the requirement of positive numbers and with a sum equal to 1. In addition, the parallelism of the paths implies that they must commute with respect to the multiplication.

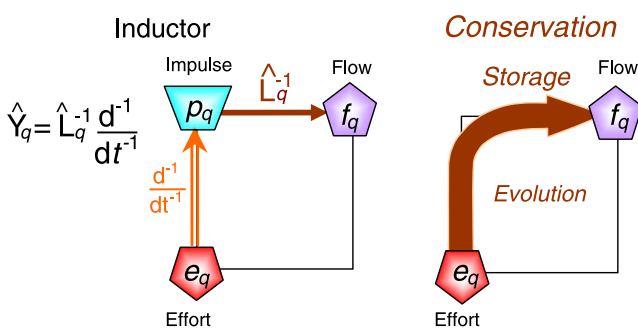
The constraint of having a constant sum of weights corresponds to conservation of energy through the paths complement: Neither energy is created nor destroyed during the operation (dissipation, i.e., conversion into heat, is not considered as destruction).

Applied to admittances, the paths complement is written

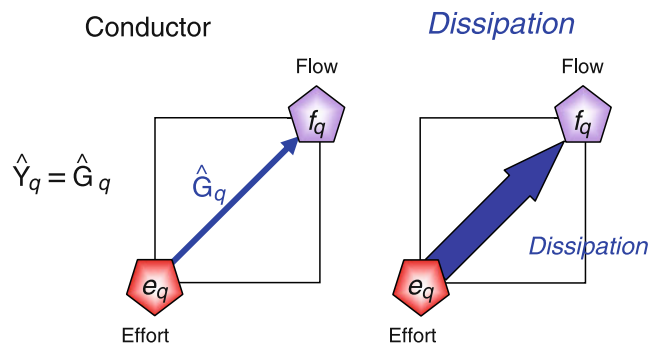
$$\text{Total Admittance } \hat{Y}_q = (\hat{Y}_{q1})^\rho (\hat{Y}_{q2})^{1-\rho} = (\hat{Y}_{q2})^{1-\rho} (\hat{Y}_{q1})^\rho \tag{16}$$

In the case of a purely capacitive path in parallel with a purely conductive path, if  $\rho$  is the weight of the capacitive path, one finds

$$\hat{Y}_q = \left( \frac{d}{dt} \hat{C}_q \right)^\rho (\hat{G}_q)^{1-\rho} \tag{17}$$

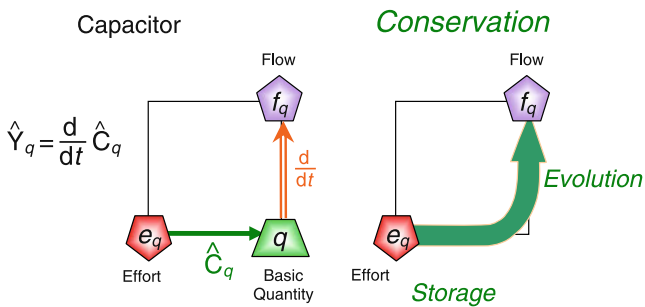


**Graph 3** Generalized inductor viewed according to three representations: algebraic formula (left), Formal Graph with elementary links (center), and Formal Graph with the composed path describing the energetic behavior (right)



**Graph 4** Generalized conductor viewed according to three representations: algebraic formula (left), Formal Graph with the elementary link (center), and Formal Graph with the composed path describing the energetic behavior (right)





**Graph 5** Generalized capacitor viewed according to three representations: algebraic formula (left), Formal Graph with elementary links (center), and Formal Graph with the composed path describing the energetic behavior (right)

A capacitive time constant playing the role of scaling time is defined as the combination of the resistance with the capacitance

$$\text{Time Constant (Capacitive)} \quad \tau_{Cq} \stackrel{\text{def}}{=} \hat{C}_q \hat{R}_q \stackrel{\text{lin}}{=} R_q C_q \quad (18)$$

Naturally, when operators are scalars (linear case), this time constant is a scalar, but when it is not the case, it is assumed that the result of the operator combination is also a scalar, as it is observed in ideal systems. By rearranging its expression, the admittance, is now written

$$\text{Capacitive – conductive admittance} \quad \hat{Y}_q = \frac{d^p}{dt^p} \tau_{Cq}^p \hat{G}_q \stackrel{\text{lin}}{=} G_q \tau_{Cq}^p \frac{d^p}{dt^p} \quad (0 \leq p \leq 1) \quad (19)$$

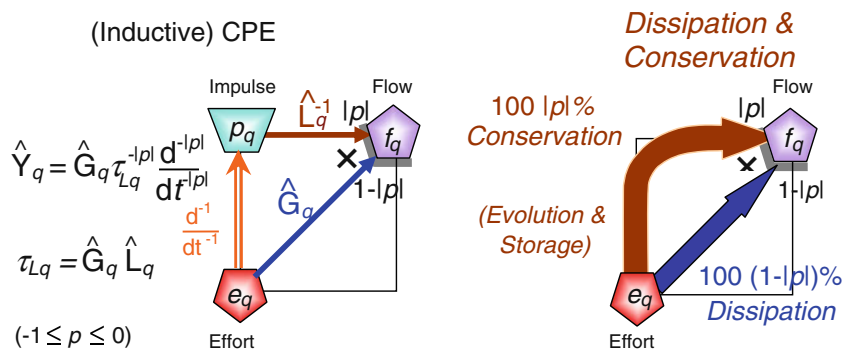
The same reasoning applies to the inductive CPE. Its admittance is written

$$\begin{aligned} \hat{Y}_q &= \left( \hat{L}_q^{-1} \frac{d^{-1}}{dt^{-1}} \right)^p \left( \hat{G}_q \right)^{1-p} \\ &= \left( \hat{G}_q \right)^{1-p} \left( \hat{L}_q^{-1} \frac{d^{-1}}{dt^{-1}} \right)^p \end{aligned} \quad (20)$$

The inductive time constant is defined as

$$\text{Time constant (Inductive)} \quad \tau_{Lq} \stackrel{\text{def}}{=} \hat{G}_q \hat{L}_q \stackrel{\text{lin}}{=} G_q L_q \quad (-1 \leq p \leq 0) \quad (21)$$

**Graph 6** Generalized inductive CPE viewed according to three representations: algebraic formulas (left), Formal Graph with elementary links (center), and Formal Graph with composed paths describing the energetic behavior (right). The two paths are composed with different weights  $|p|$  and  $1-|p|$  through multiplication on the flow node ( $p$  is negative for an inductive CPE)



The expression of the admittance of the inductive CPE is therefore

$$\text{Inductive – conductive admittance} \quad \hat{Y}_q = \hat{G}_q \tau_{Lq}^{-p} \frac{d^{-p}}{dt^{-p}} \stackrel{\text{lin}}{=} G_q \tau_{Lq}^{-p} \frac{d^{-p}}{dt^{-p}} \quad (0 \leq p \leq 1) \quad (22)$$

This achieves the demonstration of the correctness of the Formal Graph representation of a CPE as a complement between two parallel paths.

**Energetic behavior**

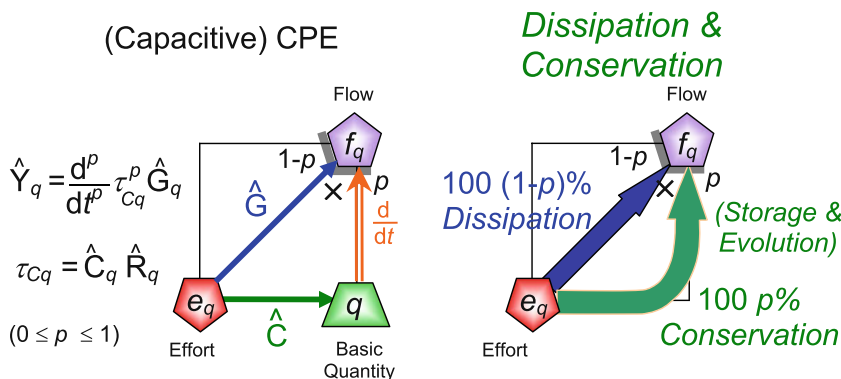
The interesting specificity of this new representation lies in the difference of energetic behavior between the two paths. One path is conserving energy because it is composed of evolution and storage, while the other is dissipating energy. Since the exponent  $p$  represents the weight of the conservation path and  $1-p$  the weight of the dissipation, one has access to a physical meaning of this quantity that can be called “energetic mode.” The scheme in Fig. 3 gives the proportion of energy that is conserved in a CPE (which corresponds to a yield) as a function of this energetic mode  $p$ .

The above scheme may induce the false perception that a continuous evolution of the exponent  $p$  (energetic mode) is possible in a CPE. The strict definition of a CPE is contained in its naming, meaning that the angle must be a constant. In this respect, another more customary scheme adopting the Fresnel representation of a vector is given in Fig. 4. It shows the connection between the angle made by a vector of constant magnitude, called director, with a horizontal axis, and the energetic behavior of a CPE.

**Connection with electrochemistry**

The previous developments were made in a general frame which applies to any energy variety. It shows the universality of the approach which is independent from the domain of application. It is time to specialize our reasoning to the case of electrochemical analysis.

**Graph 7** Generalized capacitive CPE viewed according to three representations: algebraic formulas (*left*), Formal Graph with elementary links (*center*), and Formal Graph with composed paths describing the energetic behavior (*right*). The two paths are composed with different weights  $1-p$  and  $p$  through multiplication on the flow node ( $p$  is positive for a capacitive CPE)



The link between the two energy varieties, electro-dynamics and physical chemistry, is ensured by the Faraday relation, which states that charge and substance amount of a charged species, an ion, are proportional. The proportionality factor is the product of the charge number  $z$  of the ion times the Faraday constant  $F$

$$Q = zF n \tag{23}$$

Applied to an E mechanism involving a transfer of  $n$  electrons, the charge number  $z$  must be replaced by  $n_e$  in counting positively this number in oxidation. The corollary of this relation is the link between substance flow (mass flux) and electric current

$$I = n_e F \mathfrak{S} \tag{24}$$

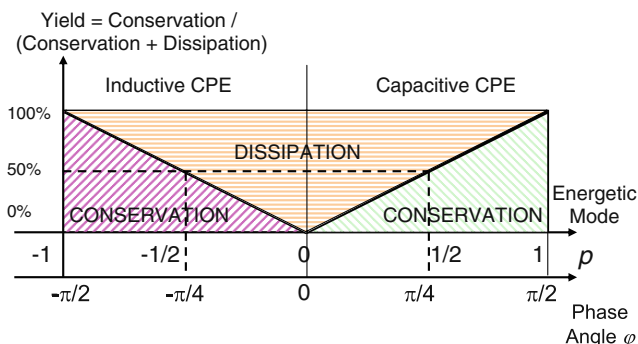
The Faraday relation induces the definition of a *translated chemical potential* (from electro-dynamics)  $\mu_V$  which is the electric potential  $V$  seen on the physical chemical side

$$\mu_V = n_e F V \tag{25}$$

Added to the chemical potential of the species, it forms the well-known electrochemical potential

$$\bar{\mu} = \mu + \mu_V \tag{26}$$

However, the process responsible of the analytical response on the physicochemical side is not a global

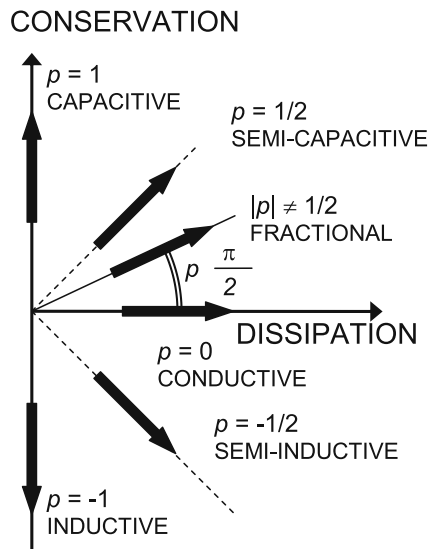


**Fig. 3** Dependence of the yield of the mass transfer (proportion of conserved energy) upon the exponent  $p$  (“energetic mode”) or the phase angle in a constant phase element (CPE)

process described by state variables and operators applied to the whole system, as we have used until now. Mass transport and charge transfer are space localized processes that require localized variables and operators for being modeled. The volumic concentration  $c$  and the substance flow density  $\mathbf{J}$  are such localized variables, and the heterogeneous intrinsic charge transfer rate  $k_{CT}^0$  and mass transfer rate  $\hat{m}$  are such space reduced operators.

Charge transfer operator

The kinetic of the charge transfer is featured by a forward heterogeneous rate constant  $k_A$  and a backward one  $k_B$  (mass transfer rates, heterogeneous rates, and flow densities are vectors rigorously speaking).



**Fig. 4** Fresnel representation of the director of a constant phase element. The angle of the director is the phase angle and its two projections on the orthogonal axes give the amount of conservation (*vertically*) and the amount of dissipation (*horizontally*)

The intrinsic charge transfer rate  $k_{CT}^0$  is defined as the common value taken by  $k_A$  and  $k_B$  when the electrode potential is equal to the standard potential. This allows simplifying the charge transfer modeling by defining an apparent concentration  $c$  mixing the concentrations of species A and B

$$c = \frac{k_A}{k_{CT}^0} c_A^0 - \frac{k_B}{k_{CT}^0} c_B^0 \tag{28}$$

so as to write the kinetic equation of the charge transfer under the form of a constant scalar operator applied to a single variable

$$J = k_{CT}^0 c \tag{29}$$

The advantage of this approach is to be extremely general, without having to detail a model of charge transfer kinetics (Butler–Volmer, Marcus...).

Mass transfer operator

The second operator  $\hat{m}$  is not very well-known among electrochemists, although introduced several years ago [1, 2]. It models all mass transfers in a single operator defined as relating a concentration difference between two locations or two moments. In case of transfer ensured by transport, the two locations are the site of the charge transfer and the bulk; in case of transfer in absence of transport (immobilized reagents, ultrathin layer), the two moments corresponds to time  $t$  and to the initial time ( $t=0$ )

Mass transfer operator  $J = \hat{m}(c^0 - c^*) \tag{30}$

The density of the substance flow (mass flux density) is related to the substance flow through a surface integration (that amounts using a surface operator), also called surface collecting.

Surface collecting  $\mathfrak{S} = \hat{A} \times J = \int_S J \times dA \tag{31}$

Naturally, when the electrode surface is homogeneous, this integration can be expressed as the product of the area with the substance flow density.

In this energy variety, the capacitive relationship is an exponential function [8]

Physicochemical capacitance

$$n = \hat{C}_n \mu = n^\ominus \exp \frac{\mu - \mu^\ominus}{RT} \tag{32}$$

that uses two scaling variables, the reference or standard amount of substance  $n^\ominus$ , taken equal to 1 mol by

convention, and the standard chemical potential  $\mu^\ominus$  of the substance. By definition of the volumic concentration and by assuming a homogeneous volume, the relation between concentration and chemical potential is written as a simple division of the capacitance by the volume.

$$c = \frac{d}{dV} n = \frac{d}{dV} \hat{C}_n \mu = \frac{\hat{C}_n}{V} \mu \tag{33}$$

All these algebraic relationships can be translated into a Formal Graph, given in Graph 8. It uses a projection in 2D of a 3D Formal Graph built with two energy varieties that are coupled through the coupling relationships given in Eqs. 24–25. The 3D representation is required for taking into account the role of space with localized variables that are placed at levels corresponding to the geometric element on which they are defined. It must be specified that variables in the nodes must be adapted to the represented step in the mechanism. For instance, the concentration  $c$  will be taken from Eq. 28 or 30 according to the considered step.

The physical chemical admittance, not explicit on the Formal Graph, can be deduced from the sequence of links starting from the chemical potential and arriving on the substance flow. Algebraically, this gives the following combination of operators

$$\hat{Y}_n = \hat{A} \times \hat{m} \frac{\hat{C}_n}{V} \tag{34}$$

With the same method, the correspondence between physical chemical admittance and electrical admittance is algebraically written

$$\hat{Y} = n_e F \hat{Y}_n n_e F \tag{35}$$

Thus, by combining these two relationships, one gets the general expression of the electrical admittance for the mass transfer with its operator  $\hat{m}$  and for the charge transfer in replacing it by the intrinsic charge transfer rate  $k_{CT}^0$

Mass transfer electrical admittance

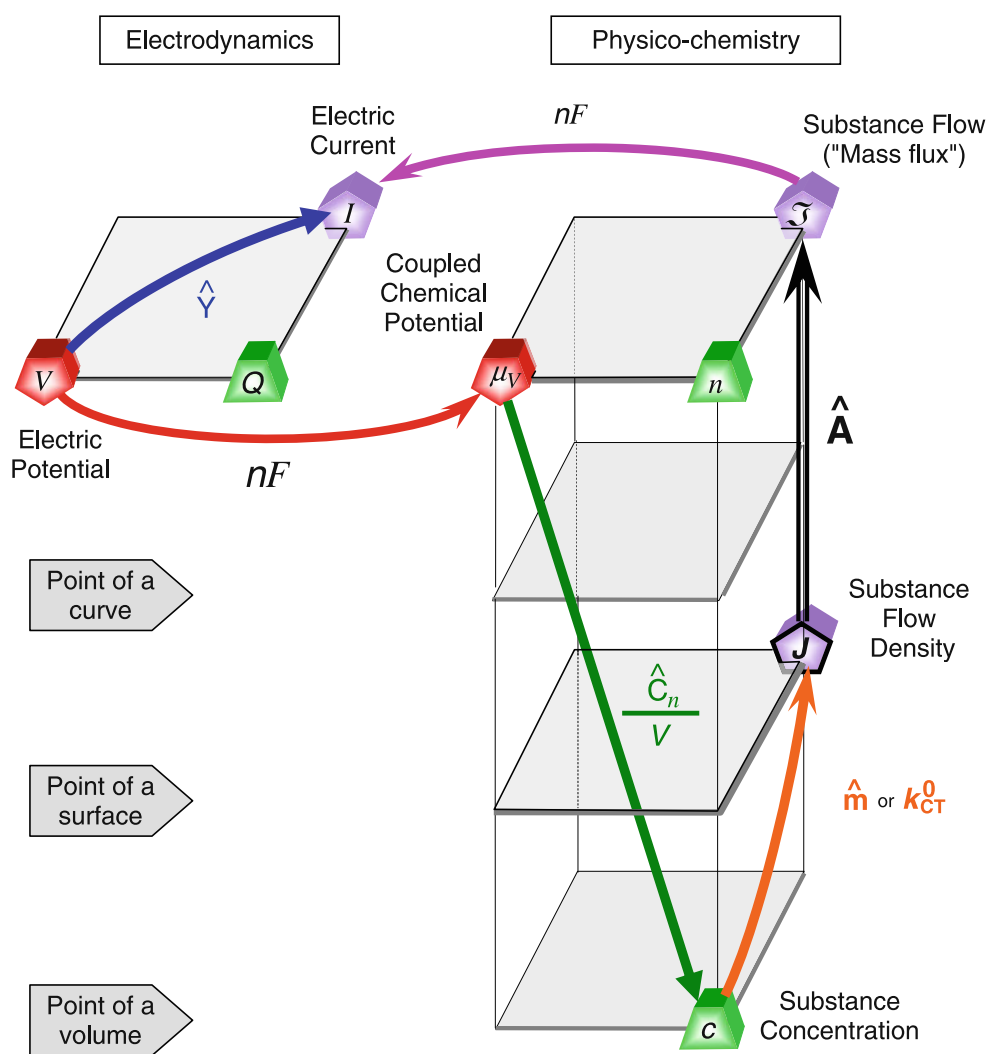
$$\hat{Y} = n_e F \hat{A} \times \hat{m} \frac{\hat{C}_n}{V} n_e F \tag{36}$$

Charge transfer electrical admittance

$$\hat{Y} = n_e F \hat{A} \times k_{CT}^0 \frac{\hat{C}_n}{V} n_e F \tag{37}$$

One of these admittances can be measured by an electroanalytical technique, when the corresponding step dominates the others in the mechanism. It is worth to

**Graph 8** Formal Graph modeling an electrical admittance as a sequence of elementary paths that are coupling relationships (Faraday relation for a transfer of  $n$  electrons, positive in oxidation), capacitive relationship (reduced by the volume), mass or charge transfer operator, and surface integration



outline that these expressions are universal models for all electroanalytical techniques whatever the perturbation used, in potential or in current or in shape. They are valid for any electrode geometry and regularity and for various mass transfers as will be shown shortly after.

In the previous Formal Graph, the translated chemical potential  $\mu_V$  has been used as participant to the capacitive relationship, which means that the hypothesis of a single step dominating the electrochemical mechanism has been done. Normally, for modeling an electrochemical reaction, a more complex picture involving all three steps of the mechanism should be drawn, by adding two more sets on the physical chemical side. However, the simplification made throughout this paper in assuming the dominance of only one step permits to ignore the non-significant ones.

It must be outlined that in case of the dominance of the charge transfer over the mass transfer steps, the previous Formal Graph keeps exactly the same structure. The only

difference lies in the substitution of the mass transfer operator  $\hat{m}$  by the rate constant of the intrinsic charge transfer  $k_{CT}^0$ , owing to the fact that the same localized variables, concentration  $c$  and substance flow density  $J$ , are linked by these operators. The main difference in behavior is that the intrinsic charge transfer rate does not depend on the time, whereas the mass transfer operator may depend directly on it, according to the regime adopted by the mass transfer.

#### Mass transfer regimes

The three basic regimes of mass transfer are listed in Table 4, with the algebraic expressions of the operators, given without demonstration (that can be found elsewhere [1, 2]). In these algebraic expressions,  $D$  stands for the species diffusivity (“diffusion coefficient”) and  $\ell$  is the thickness of the diffusion layer (stationary diffusion over a distance  $\ell$ ) or the thickness of the ultrathin layer (or the

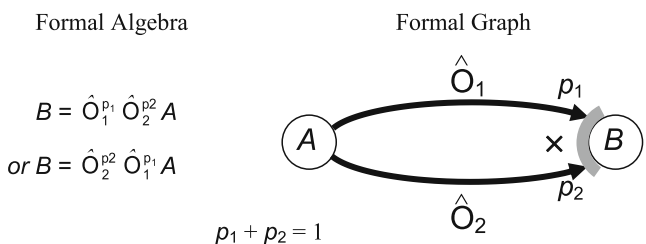
**Table 4** The three fundamental regimes of mass transfer, stationary, transient, and temporal, with their operator and their behavior in terms of conservation and dissipation of energy

Regime	Stationary	Semi-infinite transient diffusion	Temporal (ultrathin layer, immobilized species)
Mass transfer operator	$\hat{m} = \frac{D}{\ell}$ (38)	$\hat{m} = \sqrt{D} \frac{d^{\frac{1}{2}}}{dt^{\frac{1}{2}}}$ (39)	$\hat{m} = \ell \frac{d}{dt}$ (40)
Energetic behavior	Dissipation $\rho=0$	50% conservation 50% dissipation $\rho=1/2$	Conservation $\rho=1$

characteristic thickness of the layer of immobilized species). The description of the energetic behavior is made by anticipation of the analysis that reproduces the reasoning made earlier about the generalized admittance. Attribution of the dissipative behavior to the stationary regime results from the absence of time in the operator featuring the mass transfer. Normally, the simplest link between a variable in the family of basic quantities and one in the flow family uses time derivation, as for the temporal regime (ultrathin layer). When this is not the case, the path is necessarily composed with a conductance somewhere along it, which entails dissipation, even when other elementary links are storage processes along the same path. This corresponds to stationary mass transfers either ensured by diffusion or by convection or migration. Since a detailed discussion of this point can be found in a previous paper [7], we go on without demonstration.

From the observation that several forms of operator do exist for linking a concentration to a substance flow density, we deduce that some parallel paths may link these variables. By attributing a weight  $\rho$  to the path ensuring full conservation of energy and the complement  $1-\rho$  to the purely dissipative path, the mass transfer operator is formed according to the principle of path complementing introduced earlier (cf. Fig. 5)

$$\hat{m} = \left(\frac{D}{\ell}\right)^{1-\rho} \left(\ell \frac{d}{dt}\right)^{\rho} \tag{41}$$



**Fig. 5** Scheme illustrating the complement of two parallel paths and the coding used in Formal Graphs. The weights are indicated nearby the end of the arrows symbolizing the paths and the multiplication is indicated by an  $\times$ . The contour of the node is made thicker for joining the arrow ends of the paths concerned by the complement

By rearranging the right-hand side, the general expression of the mass transfer operator is obtained

$$\hat{m} = \frac{D}{\ell} \left(\frac{\ell^2}{D}\right)^{\rho} \frac{d^{\rho}}{dt^{\rho}} \tag{42}$$

This expression is valid for all cases of mass transfer in which constant repartition between dissipation and conservation is enforced (i.e., constant  $\rho$ ). It does not include varying regimes between two constant regimes, such as the ones met in a moving boundary layer (transient convection or not so thin layers with respect to the actual diffusion layer). It includes all kinds of diffusion, stationary ( $\rho=0$ ) or transient, normal ( $\rho=1/2$ ) or anomalous ( $\rho \neq 1/2$ , due to fractal medium for example), the ultrathin-layer or immobilized layer case ( $\rho=1$ ), and also processes not exclusively based on diffusion such as convection and migration of charged species that are generally stationary processes ( $\rho=0$ ).

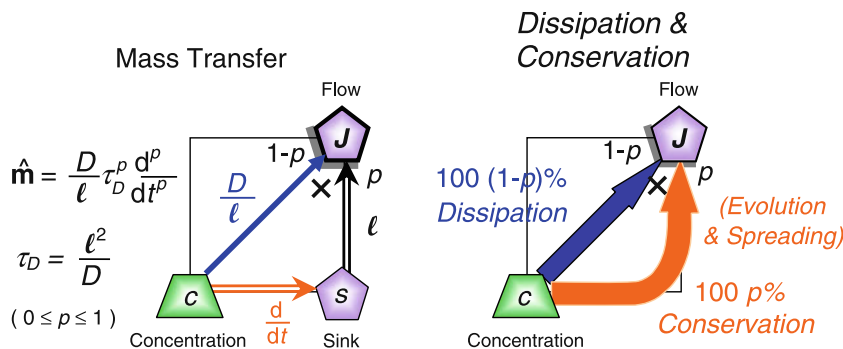
The translation into Formal Graph is made in Graph 9 by adapting the Graph 7 modeling the admittance of a capacitive CPE. An explanation needs to be given about the various elementary links met between concentration and substance flow density. The diagonal elementary link, joining directly these two localized variables, models many processes obeying to a relation using a simple vector  $u$  called mass transfer rate, or convective rate

$$\text{Convective equation } J = u c \tag{43}$$

Among these processes are found all stationary convective processes that are based either on the transport of a substance by a moving fluid, but this does not apply in solids, or on the action of a driving force or field. In this last category is found for instance the action of a gravitational field (gravitational convection), or of an electric field (migration) or of a difference of chemical potential (osmosis). The case of stationary diffusion is also included because the fundamental equation of diffusion, or Fick law,

$$\text{Fick law } J = -D \frac{d}{dr} c \tag{44}$$

**Graph 9** Mass transfer viewed according to three representations: algebraic formulas (*left*), Formal Graph with elementary links (*center*), and Formal Graph with composed paths describing the energetic behavior (*right*). The two paths are composed with different weights  $1-\rho$  and  $\rho$  through multiplication on the flow node ( $\rho$  is positive for a mass transfer)



which applies to any process involving diffusion, has for solution, in the case of stationary conditions, a simple proportionality with the difference of concentrations between two points separated by a distance  $\ell$

$$\text{Stationary diffusion } \mathbf{J} = \frac{D}{\ell} (c^0 - c^*) \tag{45}$$

This is this case which is represented in Graph 9.

The path composed with two elementary links going through the sink drawn in Graph 9 represents in fact the well-known continuity equation

$$\text{Continuity equation } \frac{d}{dt}c + \frac{d}{dr} \times \mathbf{J} = 0 \tag{46}$$

The formal graph representation decomposes this equation in two parts by employing a variable  $s$  called *sink*

$$s = \frac{d}{dt}c = -\frac{d}{dr} \times \mathbf{J} = \frac{\mathbf{J}}{\ell} \tag{47}$$

The sink variable  $s$  is defined as belonging to the flow family and as localized at the level of a point in a volume. The evolution of the concentration, expressed by the time derivation, strictly mimics the link between substance amount  $n$  and substance flow (mass flux)  $\mathcal{J}$  that are variables also related by this operator. The result of this evolution is the sink variable.

The link between this latter and the substance flow density is featured by the convergence operator, which, as signified by its name, accumulates substance in a point of the volume when flow vectors are oriented in majority toward this point (they are converging). Consequently, the physical meaning of the reverse operation, expressed by the reciprocal of the convergence, is to spread the accumulated amount in the sink, hence the proposed naming *spreading* for this operator (the creation of new names must not be encouraged but is unavoidable when one attempts to give more physical meaning to anonymous mathematical concepts). The right-hand side is obtained by making the simplifying assumption of a homogeneous space, allowing the convergence operator

(i.e., minus the divergence) to be identified with a simple division by a characteristic length.

**Conclusion**

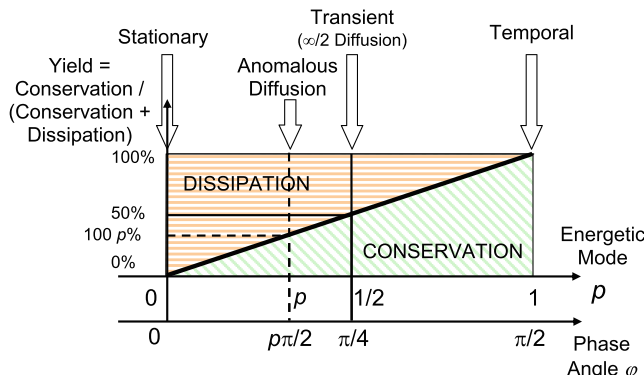
In Fig. 6 is shown the main result of this new approach, which is the correlation between the energetic mode  $\rho$ , measured by the exponent of the time derivation in an admittance (or through the phase angle in a complex admittance), and the yield of the mass transfer that quantifies the behavior of the energy in term of proportion between conservation and dissipation.

Several interesting points are emerging from this link between energetic mode and energy behavior:

The only mass transfer mode that integrally conserves energy during the process is the temporal mode (ultrathin layer, immobilized species), corresponding to the highest value of  $\rho$ , i.e., one.

The worst mass transfer mode, as regards the yield, is the stationary mode. It dissipates all the energy during the process.

Transient semi-infinite diffusion is an equilibrated process since half of the energy is conserved and the other half



**Fig. 6** Dependence of the mass transfer yield (proportion of conserved energy) upon the exponent  $\rho$  (“energetic mode”) or the phase angle, for all modes of mass transfer

dissipated. In view of a classical model of this process, based on the Brownian motion of particles, the conservation of energy corresponds to the occupancy of void sites and dissipation comes from inelastic collisions between molecules. In homogeneous media, there are no reasons for privileging one process or the other.

Anomalous diffusion occurs when this equilibrium between conservation and dissipation cannot be ensured by the system. Irregular media or interfaces, in term of geometry, are known for being responsible of fractional exponents in many processes. Fractal geometries are often invoked as the source of this behavior [11, 12], but in view of the present study, another point of view can be proposed that relies on the possible reasons for privileging a conduction process in the detriment of a conservative process using a spreading (opposite process to convergence) of molecules. In other words, this opens the way for searching more on the side of dynamic processes (conduction vs. spreading) than on the side of static geometry.

At last, the most interesting result of this graphic approach is the simplicity of the tool given to the experimentalist for interpreting his/her electroanalytical measurements. No need of a computer equipped with sophisticated solvers for accessing to this important parameter which is the yield of the process. The distance between the raw experimental result and the physical

significance is seriously shortened by this powerful tool that is the Formal Graph language.

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