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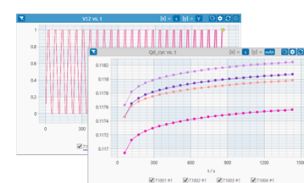
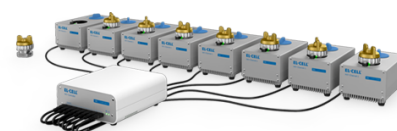
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Correlation between Electrochemical Relaxations and Morphologies of Conducting Polymer Dendrites

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Conducting Polymer Dendrites (CPD) can engrave sophisticated patterns of electrical interconnects in their morphology with low-voltage spikes and few resources: they may unlock *in operando* manufacturing functionalities for electronics using metamorphism conjointly with electron transport as part of the information processing. The relationship between structure and information transport remains unclear and hinders the exploitation of the versatility of their morphologies to store and process electrodynamic information. This study details the evolution of CPD's circuit parameters with their growth and shape. Through electrochemical impedance spectroscopy, multiple distributions of relaxation times are evidenced and evolve specifically upon growth. Correlations are established between dispersive capacitances of dendritic morphologies and growth duration, independently from exogenous physical variables: distance, evaporation or aging. Deviation of the anomalous capacitance from the conventional Debye dielectric relaxation can be programmed, as the growth controls the dispersion coefficient of the dendrite's constant-phase elements relaxation. These results suggest that the fading-memory time window of pseudo-capacitive interconnects can practically be conditioned using CPD morphogenesis as an *in materio* learning mechanism. This study confirms the perspective of using electrochemistry for unconventional electronics, engraving information in the physics of conducting polymer objects, and storing information in their morphology, accessible by impedance spectral analysis.

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Consumer electronics was so disruptive in the last decades that our lives are now greatly influenced by our relationship with internet-of-things and artificial intelligence.¹⁻⁴ COVID pandemic particularly showed that organizational schemes heavily rely on electronics to promote remote activities, that its demand will keep increasing, and that global economy strongly relies on its manufacturing/retailing.⁵⁻⁸ Its production is highly centralized and global, which generates lots of supply traffic and overcapacities to prevent future shortages.^{9,10} Its development is not strictly driven by resources' cost and sizes with the global demand.¹¹ Therefore, electronics' environmental footprint is not optimized at all: (1) Manufacturing is environmentally very expensive: circuits poorly value biomass and use precious or rare metals in their highest purity.¹²⁻¹⁴ Pricings are not directly correlated with energetical cost for manufacturing,¹⁵ material resources,¹³ nor water consumed by production facilities.¹⁶ (2) Production is excessive and not personalized: downscaling electronic technologies secured overproduction over the years of highly standardized batches of devices with largely oversized capability features (memory, processors and sensors) in regards to practical uses.¹⁷⁻²⁰ (3) Items life-cycle is too poor: devices are frequently discarded when considered obsolete in regard to newer released versions, or may be designed to diminish their lifespan on purpose to encourage consumption.²¹ Recycling is often more expensive than producing from raw materials.²²⁻²⁴ Most of these issues related to resource consumption and pollution in electronics are to be correlated with the latency of production and retailing circuits, the constant evolution of innovations and demands, and the inability of electronic hardware to physically adapt to the personal needs of individual end-users in an application. While software can upgrade by itself with very minor impacts, conventional electronics is not generative, transformative nor transient.²⁵⁻³¹ In nature, living organisms universally adapt to their environment, multiply and evolve during their life and through many generations. Sessile organisms, having no ability to move by themselves, physically extend and branch out, scavenging natural resources necessary for their development in their environment.³² Roots, mycellia, lichens or corals grow on diverse substrates to adapt

their topology and self-optimize to metamorphic structures, resilient to environmental variations.^{33,34} Metamorphism is not intrinsic to growth (organisms may adapt by orientating)³⁵, but those having the ability to fabricate tissues and evolve are true demonstrations of the existence of physical mechanisms enabling *in operando* hardware fabrication from environmental resources, and can be seen as a genuine expression of natural intelligence. The relationship between topological plasticity and inference is also a characteristic of the brain, which activates the fabrication of new synapses and dendrites on specific areas depending on our behavior.³⁶⁻³⁸

If the brain functioning has often served as inspiration for revisiting electronic architectures to achieve higher performances,³⁹⁻⁴¹ topological materials compose very few technologies for unconventional computing,⁴²⁻⁴⁶ despite their perspective to offer other solutions than improved computation.⁴⁷⁻⁵⁷ For instance, electronic devices do not self-repair, heal, multiply or compost in ambient. On the hypothesis that metamorphic electronics could potentially diminish electronics' environmental footprint by enabling these natural functionalities, one may question how signal transport in a substrate material that carries both electricity and matter could condition the information processing. As mass-driven mechanisms like convection and diffusion are very distinct from the electrostatic and electrodynamic principles governing charge carrier transport in silicon, one may expect completely different intrinsic processes in metamorphic junctions. Of a prior importance, it is necessary to identify these processes limiting signal transport in a physically evolving junction. In this study, the physical impact of conducting polymer dendrites' (CPD) morphogenesis is correlated to the impedance between electrodes as a mechanism to program an electrical system.

The CPD hold a tremendous potential in numerous applications, including healthcare because of PEDOT:PSS biocompatibility, consumer electronics as a way to save resources, neuromorphic computing for the implementation of physical neural networks using their inherent memory effects, and finally object identification because of their unique morphologies.⁵⁸ In the literature, CPD have been generated at low electric-field from electrodynamic monomers' oxidation in electrolytes.⁵⁹⁻⁶³ They adopt various shapes according to the nature of an electric signal dissipated in an electrolyte.⁶⁴ More specifically, it has been shown that CPD can grow in water and that their morphology (number of branches and

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thickness) is the product of several characteristics of the growth voltage, such as frequency, duty cycle and offset^{65,66}. The resulting topology defines a specific conduction path for flowing electrons and charging ions.^{67–69} Made of organic mixed ionic-electronic conductors (OMIEC),^{70,71} their behavior is more complex than metals:^{72–74} carrying both electrons and ions, they behave as electrochemical transistors, with the latency of charges varying for different ions. In addition to the rich morphologies at different scales and the involvement of particles in their growth,^{66,75} a multi-physical origin of mass transport is expected: this study investigates on the link between transport and morphogenesis via electrochemical impedance spectroscopy (EIS).

Experimental

Materials and methods.—Chemicals were purchased from Sigma Aldrich and have been used as such without further purification. Sodium polystyrene sulfonate (NaPSS) was used as an electrolyte at 1 mM concentration in deionized water. 3,4-ethylenedioxythiophene (EDOT) was used as a monomer undergoing oxidative electropolymerization: it was introduced at 10 mM prior solubilizing NaPSS as a surfactant. Parabenzoquinone was used equimolar as a proton scavenger and as an oxidizing agent to balance to electroneutrality upon electropolymerization. The growth was performed freestanding in the electrolyte drop on 25 μm diameter gold wires cut from a spool purchased from Goodfellow. Every experiment uses freshly cut wires approximately 1 cm long.

The plastic container is custom-made in order to prevent evaporation of volatile species in the electroactive solution, designed to hold 20 μL of solution during up to one hour in ambient in a single experiment. A view of dendrites grown in standard conditions is provided in Fig. 1b.

Impedance characterization.—EIS was performed using a Solartron Analytical (Ametek) impedance analyzer in a 2-electrode setup, either intermittently or when both dendrites reach the state where the nearest distance between them is 40 μm (a picture of the setup is shown in Fig. 1a).

Unless specified otherwise, the impedance spectra are obtained using ten samples per decade over the frequency range of 1 MHz to 100 mHz with an AC magnitude of 10 mV_{rms}. The DC bias is 0 V. The sampling rate and wave amplitude were set to minimize artifacts of voltage non-linearity and temporal drift. Except if mentioned otherwise, the time indicators on each label for impedance measurements define the total growth time of the CPD, rather than the practical duration of an experiment, which is characteristic of CPD aging.

Distribution of relaxation times.—The interpretation of the EIS is often challenging, especially when the physical mechanisms are complex and numerous. One way to help with the analysis is to use the Distribution of Relaxation Times (DRT) method, a powerful tool used on complex impedance data to separate and characterize the relaxations in an electrochemical system⁷⁶. The DRT has been

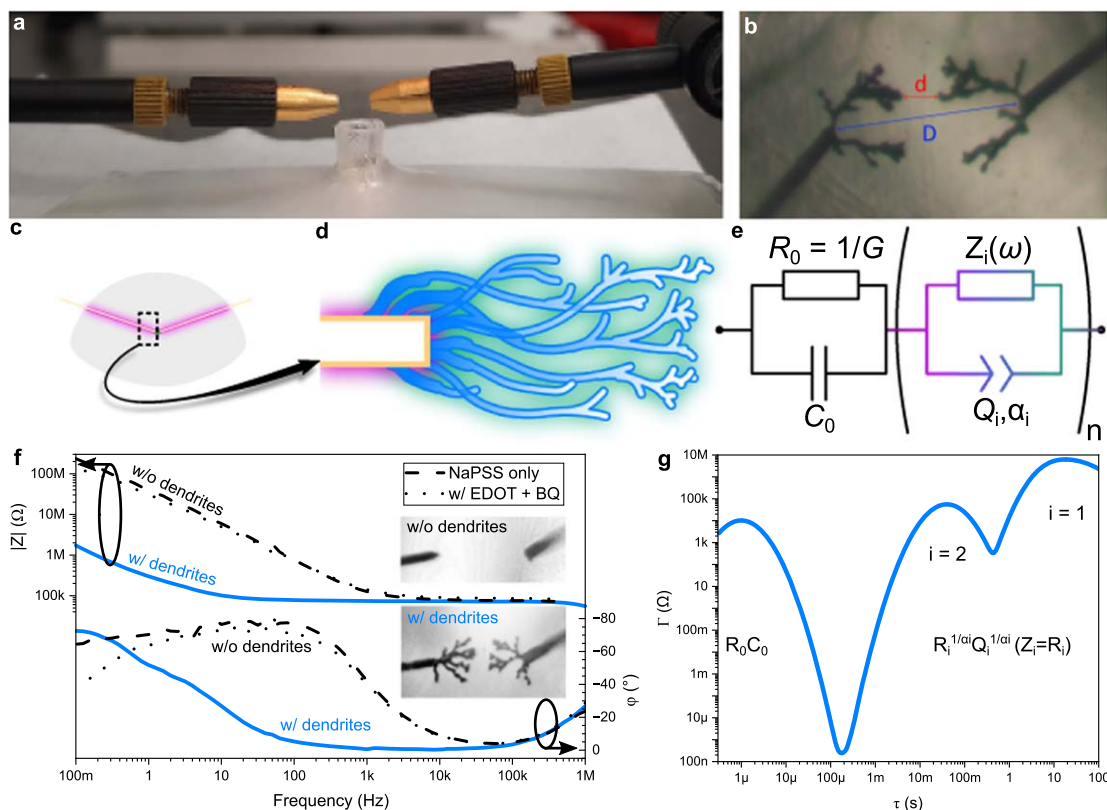


Fig 1. Experimental setup and determination of an equivalent circuit model **a**, Free-standing 2-electrode setup to generate conducting polymer dendrites. Two micromanipulators are placed on the sides of the plastic container. Each supports one gold wire. The container is filled with 20 μL of solution. A camera placed vertically above the container helps positioning the tips of the wires 240 μm distant from each other. It also helps monitoring the reaction while it is taking place. **b**, Optical image of an incomplete dendritic connection. *d* designates the nearest distance between the tips of the dendrites while *D* is the distance between the tips of the gold wires. **c**, A schematic of the wires at the centimeter scale. The electrolyte is coloured in gray, while the surface of the wires in contact with the electrolyte is in purple. **d**, Zoomed-in representation of the tip of the wires, at the micrometer scale. The dendrites are drawn in blue, the surface corresponding to the interface between polymer and electrolyte is shown in green. **e**, The proposed equivalent circuit containing a RC element to modelize the electrolyte's contribution to the impedance and a variable number of ZARC elements to modelize the interfacial phenomena. $Z_i(\omega)$ is intentionally left as generic as possible but $Z_i = R$ is considered for the fittings in this paper. **f**, Bode plots in magnitude and in phase of the uncoated wires in NaPSS only and in the full growth electrolyte (EDOT + NaPSS + BQ). In solid blue, Bode plot of the dendritic interconnection immersed in the growth electrolyte. The pictures of the wires with and without electrolyte are also shown. **g**, Distribution of Relaxation Times of the dendritic interconnection shown in Fig. 1f.

applied in numerous areas, such as fuel cells,^{77,78} batteries,^{79,80} and sensors,⁸¹ providing insights into specific reactions, charge transfers, and limiting processes in solution. The characteristics of the peaks—such as width, height, x-coordinate, and symmetry—can give hints about the duration, ideality, homogeneity of each process, and its relative impact on the current.⁸² Unlike EIS fitting, the DRT does not require a specific equivalent circuit model to fit the impedance data to, as it is purely a transformation from the frequency to the time domain, but assumes that the system can be approximated by an infinite series of R/Q elements. The equation it is trying to solve is given in Equation 1⁸³,

$$Z(\omega) = R_{\infty} + R_p \int_0^{\infty} \frac{\gamma(\tau)}{1 + j\omega\tau} d\tau \quad [1]$$

where τ is the relaxation time, ω the angular frequency, R_p the polarization resistance, R_{∞} the high-frequency resistance limit and γ the distribution of relaxation times. As it is an ill-posed inverse problem, the smallest perturbation in the impedance (for example, noise in the measurement) can have a considerable impact on the result of the inversion. Therefore, the DRT requires careful parameter selection⁸⁴. Particularly in regularization, a process which can smooth the DRT profile and potentially lead to loss of information. Regularization is essential for controlling noise and preventing artifacts such as artificial peaks without a physical meaning.⁸⁵

Circuit modeling and DRT parametrization.—Circuit modeling was achieved using ZView ver. 3.2b. The DRT analysis was performed in Python using pyDRTTools⁸⁶ and the following set of parameters:

Method of discretization:	Gaussian	Regularization derivative:	2 nd order
Parameter selection:	mGCV	Regularization parameter: (λ)	0.01
RBF Shape Control:	Shape Factor	FWHM Control	1.0

This set of parameters was used in all DRT analyses shown in this paper. The modified generalized cross-validation (mGCV) method was chosen as an effective way to determine the value of the regularization parameter λ ⁸⁴. The resulting DRT profiles are consistent with the Nyquist plots in terms of number of relaxations and timescales. Finally, the deconvolution of the DRT peaks, although a very powerful means to help separate the processes and investigate their physical origin, was not pursued in our case as no useful information could be extracted through it.

Results and Discussion

Multiple relaxations and equivalent circuit.—EIS was already performed on dendrites^{66,72,87,88}. In the case of two gold wires supporting two distinct CPD, a clear non-Debye relaxation is observed.^{72,88} Despite the fact that impedance is highly dependent on the CPD morphology grown at the apex of both gold electrodes, the influence of the wires on the signal propagation has not been established.⁷² Later, the impedance from CPD@Au to a naked silver wire showed a more ideal discharge with respect to Debye's relaxation, which highly depends on the voltage bias applied through the CPD during EIS:⁸⁷ as PEDOT:PSS is a material which can be electrochemically doped or dedoped, the charge transport through the dendritic structure can affect the conductance of the polymer object, hence the charge distribution at the CPD/electrolyte interface. In our case, to analyze the properties of CPD with minimal dependence on the setup (such as voltage bias or the nature of the counter electrode), we chose to study the signal propagation from one dendrite to another without applying a voltage bias ($V_{DC} = 0$). Figures 1c, 1d show two wires used in the experiment with at their tip a dendrite. Both are immersed in a 20 μ L volume of water contained in a plastic container. Different colors are used to

distinguish the three existing interfaces between ions and electrons: a metal-electrolyte interface (purple), a polymer-electrolyte interface (green) and the OMIEC as heterojunction of ion-conducting semiconducting polymers (blue).

Despite conducting polymers being low mobility semiconductors, the hole dynamics in PEDOT are faster than the ion drift mobility in water,⁸⁹ so the slow dynamics of the ions dictate the overall dynamics of the system. As ions have different natures (size, charge, electro/nucleophilicity) and interfaces have different properties (roughness, surface, permittivity of the ion domain), it is expected that the junction limits signal propagation at different cutoff frequencies according to the different relaxations involved with the multiple ions and interfaces (Fig. 1e depicts a generic equivalent circuit assuming that all n+1 relaxations can be modeled in cascade form, one wire to the other). Figure 1c, 1d illustrates the difference in scale of these interfaces and that dendrites only represent a small domain of the electrochemical system. In order to assess the independence of an impedance spectrum to the environment of the CPD (the wires that support them, and the redox species that surround them), three comparisons are presented in Fig. 1f on the same Bode plot. The impedance of a pair of gold wires immersed in an electrolyte containing only NaPSS_(aq) is compared to its impedance after introducing EDOT_(aq) and BQ_(aq) (the total volume of electrolyte is reduced to the same volume prior to the introduction of EDOT_(aq) and BQ_(aq) in NaPSS_(aq)). A minor but noticeable contribution of EDOT and BQ can also be seen at low frequency in the spectrum. The magnitude remains too high for it to explain the increased conductivity after deposition. Thus, we can conclude that the interactions between EDOT, BQ and the gold wires do not limit the impedance of the system: nor by a faradaic process (electroplating *in operando*) or by affecting the diffuse layer at electrode/electrolyte interfaces. The impedance of these same wires is compared to the one after electropolymerizing two CPD of comparable morphologies, using standard growth parameters (100 Hz, 50% duty-cycle and 0 V offset). The modification results in a drastic change of the impedance property of the system, by a decrease of at least two orders of magnitude of the impedance modulus (Fig. 1f). The resulting spectrum confirms that relaxation processes in polymer electrolytes can have characteristic time constants on the order of seconds.^{90,91} Despite the fact that dendrites represent only a small fraction of the volume of the wires immersed in solution, CPD define most of the electrodes' impedance after growth, showing that the setup is suitable to study the impact of a CPD morphology on the impedance independently from the system. Another advantage of the freestanding wire setup is that no substrate is in contact with the electrodes: studies have shown that a CPD growth can be impacted by the affinity of a dendrite on a flat surface.⁶¹ As the phase of the signal appears to be rather complex, it is assumed that multiple relaxations rule the impedance modulus drop from 100 mHz to 1 kHz.

In order to assess it, the distribution of relaxation times (DRT) is performed assuming an elementary decomposition of the system in discrete Voigt elements in series (Figs. 1e, 1g). The range of the impedance characterization is enlarged from 1 MHz to 10 mHz to ensure that all relevant peaks can be visible in the DRT. The distribution of relaxation times allows to visualize the number of processes taking place in the system without prior knowledge of its physics. Figure 1g shows multiple relaxations. The highest frequency peak occurring at $\tau(R_0, C_0)$ or $\tau_0 \approx 1 \mu$ s could be attributed to the dipolar polarization of the solvent (we observe in general that this relaxation is invariant with the growth for any morphology, except when CPD merge and bridge one another). The other time constants are however very dependent on the growth conditions. They represent interfacial phenomena that are at this point difficult to interpret physically in the current stage, as the complex morphology and chemistry come into play. It can be noted that the lowest frequencies processes are especially slow ($\tau_2 \approx 30$ s), which contrasts with the idea one might have for a RC system of such small dimensions ($D = 240 \mu$ m, $d = 40 \mu$ m). The peaks in the distribution

Table I. Parameters for the dendrites grown in Fig. 1.

$1/G(k\Omega)$	$R_1(M\Omega)$	$Q_1(nF \cdot s^{\alpha_1-1})$	α_1	$R_2(k\Omega)$	$Q_2(nF \cdot s^{\alpha_2-1})$	α_2
76.597	19.012	803.11	0.93028	121.520	829.83	0.84246

are well spaced, distinguishable and symmetrical enough to follow a Cole-Cole distribution of two parameters α and τ .⁸³ However, given the strong dependence of the result on the discretization parameters, fitting the peaks to a Cole-Cole distribution was not attempted. The broadness of the peaks can also appear unusual as they span over multiple decades of time constants, however, this effect is reinforced by the log/log scale used in all the DRT throughout this study, that allows to see all peaks, otherwise the dominant relaxation in the low frequencies would overshadow the other existing relaxations. It is also not excluded that the regularization parameter was chosen high enough to merge close relaxations and contribute to this observed broadness. Based on the number of peaks displayed by the DRT, an equivalent circuit is defined in Fig. 1e depending on a number of n relaxations composing the system. First, an ideal R|C relaxation at $f_0 = 1/2\pi\tau_0$ due to the geometric capacitance of the system (where the frequency is too high for ion motion and where water behaves as a dielectric), is followed by numerous ZARC elements in series, for which, in Fig. 1g, $n = 2$ is chosen to modelize the longest relaxations. A preliminary fitting performed with this model (with $Z_i(\omega)$ as ohmic resistors) provides a satisfying match and results in the parameters presented in Table I.

The corresponding time constants are $\tau_1 = 18.73$ s and $\tau_2 = 0.07$ s, which are reasonably close to those obtained from the DRT. Considering the large difference in scale between both time constants, it is reasonable to assume that they are not to be attributed to one dendrite each, as their morphologies are comparable in size and features. The high values for R_1 and τ_1 indicate a long and highly resistive process, while the other ZARC element describes a relaxation several orders of magnitude faster, less resistive and also less ideal, suggesting that both relaxations originate from different physical processes, requiring deeper insight on varying the physical structure to understand the origin of the multiple processes. Finally, it is interesting to note that while R_1 and R_2 have widely different values, Q_1 and Q_2 are essentially the same. But because in practice Q and α are difficult to decorrelate, and as both α are different between the two relaxations, it is at the present stage difficult to conclude any physical meaning from this equality. In fact, the units of Q contain the value of the α parameter, being different, therefore, from each other.

Elements evolution upon morphogenesis.—Fig. 1's impedance is representative of disconnected symmetrical dendrites grown in well established, standard conditions. A number of time constants could be identified without information on the physical origin of the underlying processes. To understand this origin, the system is perturbed by several variables: the first one of interest is the stage completion under steady conditions of growth. To evaluate this effect, a set of EIS measurements is performed intermittently by interrupting a single growth at multiple stages, starting from uncoated Au wires until both dendrites interconnect. Previous tests in Fig. 1 have confirmed that EIS is not invasive and does not modify the CPD when no bias is applied. Conventional EIS cannot be performed *in operando* with the growth to characterize its impedance without faradaic processes, but intermittently interrupting a growth does not perturb the morphology by itself.⁶⁵ Such interruptions are depicted in Fig. 2a where each white edge separating different colors corresponds to a stage where impedance was measured while the system remained at rest. For this study, a new variable called T_{ep} is introduced as the time spent continuously electropolymerizing before the next impedance measurement. The choice of T_{ep} is crucial and should take into account the duration of

an impedance measurement at each step (approximately one minute per EIS) because CPD growth appears harder to trigger over time, which limits the number of possible EIS measurements over a growth. Three values of T_{ep} are tested, one for each three different growths. The dendrites in the three experiments are, while strictly different, grown under the same growth parameters (frequency, magnitude, duty cycle of the input voltage), leading to three comparable dendrites with the same features. A first growth with $T_{ep} = 10$ s is performed to observe the EIS evolution from nucleation to interconnection with 14 samples (Figs. 2a, 2d). It allows to monitor the impedance for the total duration of the growth, 140 s, with a sufficient resolution. Growth with shorter T_{ep} at 1 s (Fig. 2c) and 100 ms (Fig. 2b) were performed to observe the drastic change of impedance at the very beginning of a growth with more resolution, and are therefore stopped well before the connection is complete. Despite the three growths occurring under the same experimental conditions but leading to three distinct morphologies, a continuum is observed in the impedance decrease (Figs. 2b–2d) as the data from the three experiments were plotted together. It should be mentioned that the $T_{ep} = 1$ s and $T_{ep} = 0.1$ s series are generated at a higher AC magnitude of 50 mV_{rms} as the impedance is particularly high and noisy in the low frequency region when there is no PEDOT coating on the gold wires, leading to a current below the specifications of the current measurement units used for this study. The increase in V_{rms} during the intermittent EIS does not appear to affect the growth. It appears that most of the impedance change occurs at the very beginning of the growth: the very first milliseconds are where the magnitude in the low frequencies falls the most. The top of the phase also slightly drops and shifts toward the low frequencies. At high frequency, most of the change occurs when the distance between the wires is reduced as they get closer to each other, lowering the electrolyte's resistance $1/G$. A plateau in the 1-10 Hz range is also gradually appearing. The data of the $T_{ep} = 10$ s set, strictly reduced to the part of the experiment where the dendrites are growing but are not yet connected, are fitted with the equivalent circuit defined previously. The fitted parameters are presented Figs. 2e–2h. Two R|CPE elements are considered (subcircuits of a resistor parallel to a constant phase element), modeling the slowest relaxations. CPE_{*i*}'s impedance is given by $Z_{CPE_i}(\omega) = 1/Q_i(j\omega)^{\alpha_i}$, where Q_i is a pseudo-capacitance, $j^2 = -1$, ω the angular frequency related to the frequency f by $\omega = 2\pi f$, and α_i ($0 < \alpha_i < 1$) the dispersion coefficient.⁹² For each Voigt circuit, an effective capacitance $C_{eff,i}$ can be defined as: $C_{eff,i} = Q_i^{1/\alpha_i} R_i^{1/\alpha_i-1}$.⁹³ Interestingly, while most of the system's resistances are decreasing upon electropolymerization including the electrolyte resistance $1/G$, R_2 increases slightly. The opposite trends of R_1 and R_2 with the growth validate that both relaxations originate from different processes and are not specifically to be attributed to each dendrite distinctive morphology.⁹⁴ And while the dispersion coefficient α_1 converges toward 1.0, becoming equivalent to an ideal capacitor, α_2 quickly stabilizes around 0.8, although this behavior is not systematically observed. The three DRT in Figs. 2i–2k display actually more relaxations than previously observed: a total of four time constants despite the noise being removed by the 50 mV AC magnitude, cementing the idea that the system has four relaxations taking place with or without dendrites, and that dendrites do not create additional relaxations but rather affect the existing ones, defined as R|C₀($\tau_0 \approx 1$ μ s) and R|CPE_{*i*}($\tau_i \approx 1$ -10 s for $i = 1$, 10-100 ms for $i = 2$ and 0.1-1 ms for $i = 3$ - pointed by the blue marker for R|C₀ and respectively red, green and orange for R|CPE_{*i*} in Figs. 2i–2l). The shift toward the low frequencies previously observed in the Bode plot translates

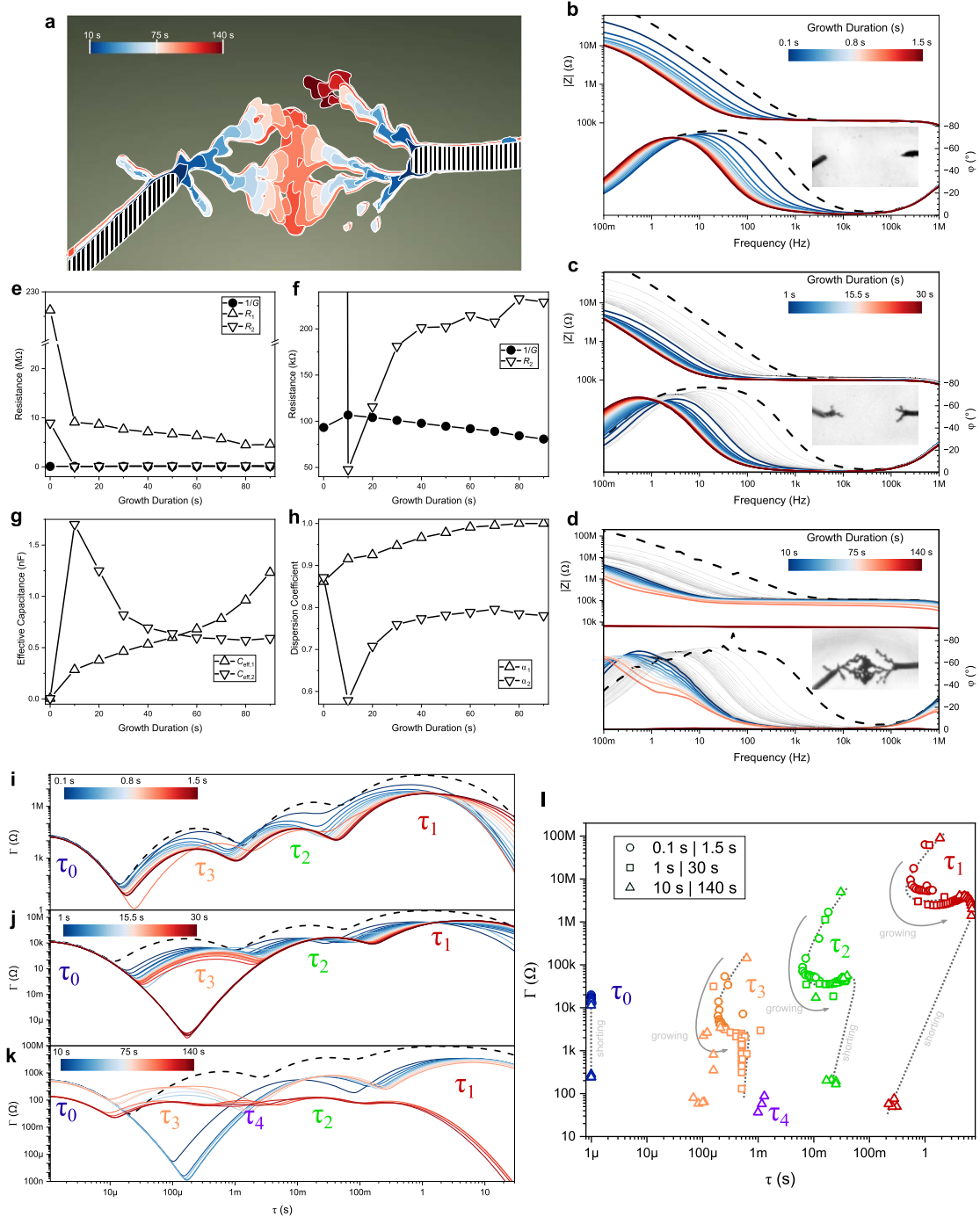


Fig 2. Impedance measurements upon growths. **a**, Vectorized-stacked images of time-lapsed pictures recorded during growth characterized in Fig. 2d. **b-d**, Bode plots in magnitude and in phase for dendrites grown from 0 to 1.5 s ($T_{ep} = 0.1$ s), from 0 to 30 s ($T_{ep} = 1$ s), and from 0 to 140 s ($T_{ep} = 10$ s). Insets: pictures of each deposition at the end of the experiment. In gray, combined impedance data of the earlier growths. **e-h**, Evolution of the fitted model parameters over growth, for the resistances (**e,f**), effective capacitances (**g**) and the dispersion coefficients (**h**). **i-k**, DRT of growths for $T_{ep} = 0.1$ s (**i**), 1 s (**j**), and 10 s (**k**). **l**, Dependency of the DRT's $\log(\gamma)$ local maxima with $\log(\tau)$.

in the time domain to a shift toward the slow relaxations, as τ_2 and τ_3 get longer over time. Meanwhile, the third $R|CPE_3$ relaxation, also subjected to this shift, tends to disappear during the growth. Considering the low value of impedance for this relaxation, the disappearance of this peak could be an effect of the regularization of the DRT. As the CPD grows and its surface area increases, the current increases for the same applied voltage, leading to a decrease of impedance over the whole medium-low frequencies region where ions have the time to reach the material. As the γ value of the τ_3 peak decreases and reaches values as low as 100 Ω , it has higher

chances to get smoothed out in the regularization. Finally, the high frequency relaxation $R|C_0$ is stable over time until both dendrites are connected, where the electrolyte's contribution to the impedance becomes minimal. The local maxima of each relaxation in the DRT are plotted in Fig. 2l for all EIS. Again, data are consistent between the sets. $R|CPE_1$, $R|CPE_2$ and $R|CPE_3$ show the same type of trajectory in the plane, rapidly stabilizing at a certain γ before their time constant gradually become longer, and finally dropping upon dendrites' completion. Only $R|C_0$ follows a straight vertical trajectory, unaffected by the dendrites' growth or the decreasing distance

between the electrodes. We note that the initial value of τ_1 is approximately 1 s and corresponds to the configuration without polymer on the wires, meaning that, already when charging at a gold interface, ions still need seconds to stabilize over a 240 μm gap in water. This stresses the fact that the dynamics of the CPD are not only conditioned by their morphology but also by the dynamics of a given electrolyte in a given environment and that a given morphology may result in very different dynamics if solvents and ions are changing (which has not been investigated at the moment). The DRT profiles of the system when the dendrites are fully connected are also displaying four relaxations in total, each being of similarly low peak values. This contrasts with the previous DRT profiles where the γ would increase with the time constants. In this configuration, no relaxation is longer than one second. An ionic contribution to the current likely still exist but is minor when compared to the electronic conduction once CPD are in contact with one another. Also, the growth itself seems interrupted, as the DRT spectra do not change substantially. However, some growth can still happen to incomplete side branches (often considered 'dead' branches, although it is a fact that they keep promoting growth). Their contribution to the impedance is overshadowed by the primary branches being fully connected, although not completely made silent on the EIS.

Decoupled effects of time and distance.—Made of a conductive material, CPD decrease systematically the electrolyte gap as the material grows during a specific time. The effect that a given morphology has on the impedance shall generically depend on the morphology itself and not the distance between vicinal dendrites, nor the time dendrites age in an electrolyte. These two parameters have been studied separately.

To study the impact of aging, measurements have been performed on an incomplete symmetric morphology without modifying their structure nor their environment (Fig. 3a). EIS is performed approximately every minute over 32 minutes in solution, as the dendrites are left as is (minor manipulations of their position have been performed to compensate an apparent wire drift happening over time). At high frequencies, the impedance remains steady by the stability of its modulus and its phase. This indicates that water composing the electrolyte does not evaporate at a significant point and that the electrolyte concentration does not change noticeably as a result. An effect at low frequencies is however noticeable in the phase plot, meaning that time has a minor impact on a dendrite's impedance. Figure 3b indicates that one of both relaxations becomes slightly more ideal overtime (however the average value of related dispersion coefficient α_2 drifts by less than 0.01 over 13 minutes). On the DRT, the R|CPE₂ relaxation trajectory in Figs. 3c, 3d is noticeably affected by aging, as τ_2 drifts toward faster relaxation times. Possible reasons explaining the aging may be related to evaporation of EDOT and BQ in solution over time, affecting more rapidly their concentration than water's evaporation, and for which a minor effect of their presence on an EIS has been evidenced in Fig. 1f.

The impact of CPD distances have been studied independently from their morphology on the same growth of CPD pair by adjusting their distance via micro-manipulators supporting the gold wires (without pulling the CPD out of the growth electrolyte). The Bode plots in Fig. 3e show that a significant drop in magnitude exists in the highest frequency region ($f > 10$ Hz), likely caused by the decrease in electrolyte resistance since the distance that ions have to cross is significantly reduced (despite their trajectory from one morphology to another being complex). The fitted values in Fig. 3f confirm that the electrolyte resistance is the parameter responsible for the high frequency variation observed in the impedance spectra in Fig. 3e. At the particular case where $d = 0$ μm and the dendrites appear in contact with each other, the magnitude is slightly dropping while the frequency increases. This likely leads to the R|CPE₃ relaxation being visible in the DRT, unlike the other cases, as shown in Fig. 3g. This behavior is the opposite of what was observed in the

previous section: the τ_3 peak now reappears when CPD are brought in contact, even though they are not bonded together. In this situation, the transport mode has not shifted drastically and the current remained mainly ionic. Assuming that τ_3 is close to being smoothed out by the regularization, a small increase of resistance could make it appear again. In this case, the increase of resistance can come from the fact that the enclosed dendrite has less surface area and more constrained conduction paths. As for the low frequencies, an effect on the phase is noticed. The trajectory of the R|CPE₂ relaxation, depicted in green in Fig. 3h, shows that R|CPE₂ is, again, the only relaxation affected by the varying gap for a given morphology. R|CPE₁ remains poorly affected by the CPD distance, which indicates that the underlying process is defined by the interface with the electrolyte on both electrodes rather than the volume of electrolyte between dendrites. It should be pointed also that because each measurement requires a specific duration for the acquisition, the set of measurements may be affected by the effect of the time has shown previously in Fig. 3a-d: it is, in fact, suspected that the slight drift at low frequency in Fig. 3e is due to aging rather than distance.

Among the multiple relaxations taking place in the system, only R|CPE₂ is yielded by a mechanism which is moderately affected by time, drifting the dispersion coefficient by less than 0.01 over 13 minutes. Distance has no effect on the impedance at the lower frequency part of the spectra where electrochemical relaxations dominate the dynamics.

Impact of the dendrite's morphology.—As the setup allows monitoring changes in a CPD impedance (Fig. 2) with a minor influence of the gold electrodes surface and electroactive electrolyte components (Fig. 1) or of the wire distance and solution aging (Fig. 3), different morphologies of CPD growth on pairs of different Au wires have been characterized to observe an impact of their fractality on the interconnection impedance (considering that different Au wires or CPD gaps would have no visible impact on the impedance). Former studies showed that varying pulse signal frequency or duty-cycle during growth affects greatly the CPD morphology.^{65,72} Because of the low concentration of anions in solution ([PSS⁻] = 1 mM) and the high voltage amplitude (5 V) applied to the wires, ions cannot screen the voltage on the whole wire entirely, and are therefore migrating from one wire to the other alternatively. Once ions have reached the apex of the dendrite (as the closest point from one CPD to the other), they start diffusing along the wire, going deeper if the frequency is low enough, leading in that case to electropolymerization on a large surface, and so to bulkier dendrites. Therefore, the amount of time spent electropolymerizing one wire will directly change the thickness and number of branches of its corresponding CPD. Considering this, dendrites were formed with five different pulse frequencies (50, 100, 150, 200, and 300 Hz) and their impedance was measured at $d = 40$ μm apart from each other. A constant delay of six minutes was introduced between adding the water in the container and taking the impedance measurement, so the drift effect is comparable from one morphology to another. Additionally, each morphology was characterized three times at specific durations for fair comparison of their respective differences in regard to the temporal drifts (Fig. 4). The resulting morphologies and Bode plots are presented respectively in Fig. 4a and Fig. 4b. The magnitude at high frequency does not exhibit a clear relationship with the frequency: it is assumed that for comparable distances d , the electrolyte conductance is dominated by the number of branches on each CPD rather than their respective thickness (this feature is less controllable than the branch thickness, changeable by varying the growth frequency)⁶⁵. The magnitude at low frequency follows a monotonous trend with the growth frequency: the higher the growth frequency, the lower the effective capacitance appears to be. This is to be attributed to the lower volume of OMIEC on thinner dendrites (grown at higher frequencies) than thicker ones (grown at lower frequencies). On the other hand, thicker dendrites exhibit lower and flatter impedance modulus

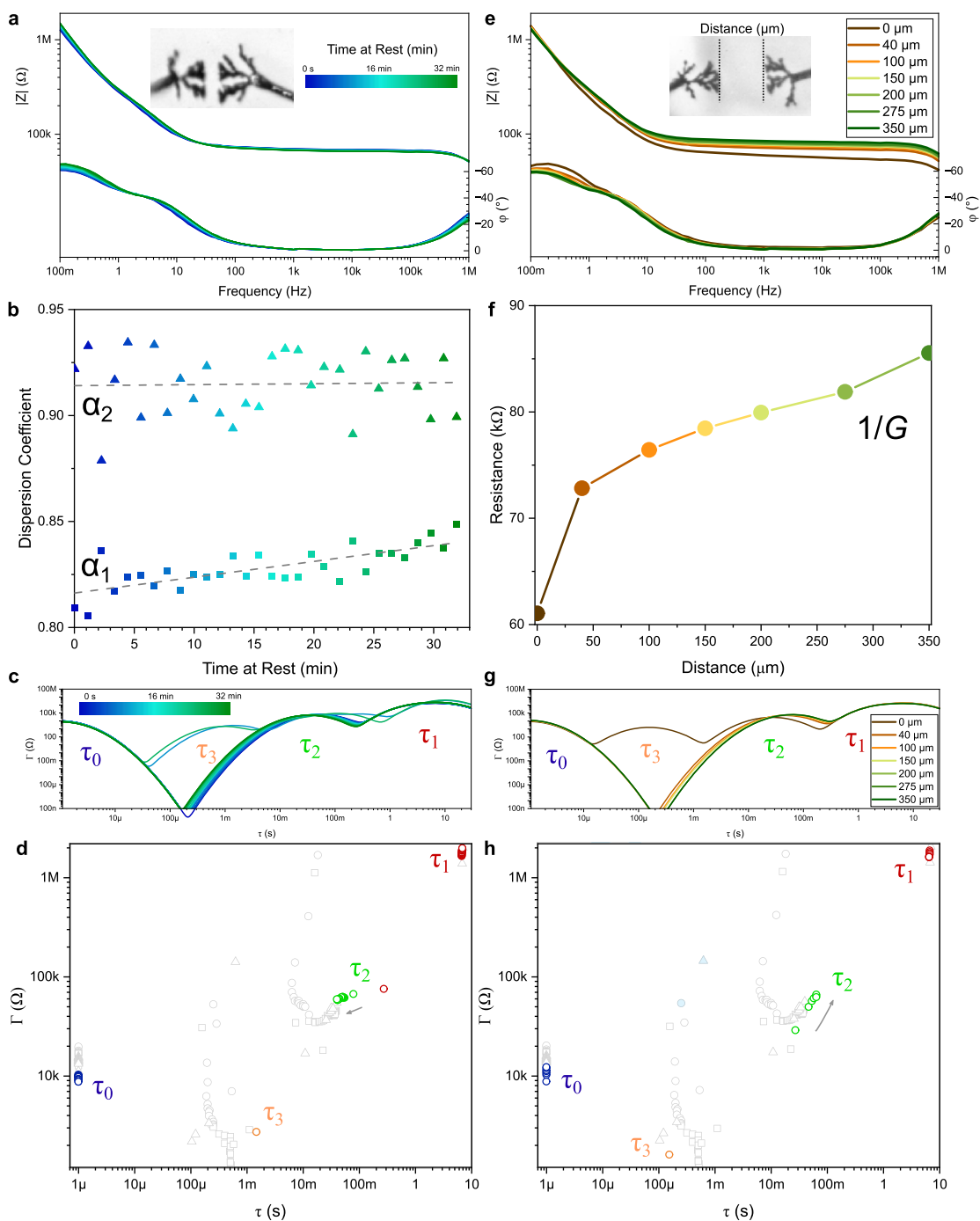


Fig 3. Dendrite stability and impact of their distance on the impedance. **a**, Bode plots in magnitude and in phase for 32 min (measured every minute). Inset: picture of the dendrites at the end of the experiment. **b**, Dispersion coefficients stability, from Fig. 3a's data fitting. **c**, DRT from Fig. 3a's data. **d**, Dependency of Fig. 3c's DRT local maxima of $\log(\gamma)$ with $\log(\tau)$ (compared to Fig. 2's data in gray). **e**, Bode plots in magnitude and in phase for different distances. Inset: picture of the dendrites 100 μm apart. **f**, Dependence of the fitted electrolyte resistance with the dendrite distance. **g**, DRT for the different gap widths. **h**, Dependence of Fig. 3g's DRT local maxima of $\log(\gamma)$ with $\log(\tau)$ (compared to Fig. 2's data in gray).

and a trend in the phase which deviates even more from the ideal -90° Debye relaxation capacitor. From the impedance data fitting (Fig. 4c), the dispersion coefficients α_1 and α_2 , initially distant from each other of about 0.2, not evolving much between 50 and 100 Hz, were shown to abruptly converge between 100 and 200 Hz toward the same value of 0.896 ± 0.001 . Incidentally, most of the morphological changes also happen below 150 Hz. As the frequency increases, dendrites become less distinguishable from their morphology, same as their respective dispersion coefficient. The DRT in Fig. 4d shows a monotonic evolution of two to three R|CPE;

relaxations with the growth frequency. As dendrites get thinner, all relaxation time constants τ_i increase. This is in line with the idea that thicker dendrites may retain longer ions in their nano-structure as an OMIEC. The local maxima of the DRT in Fig. 4e show that thinner dendrites have higher values of γ and τ_1 overall, however the interpretation of the differences in spectra here is made difficult because of the relative existence of the third relaxation, which can cause a shift in the DRT and complicate the comparison. Another effect that must be taken into account is that electropolymerization takes longer at high frequency for comparable voltage applied during

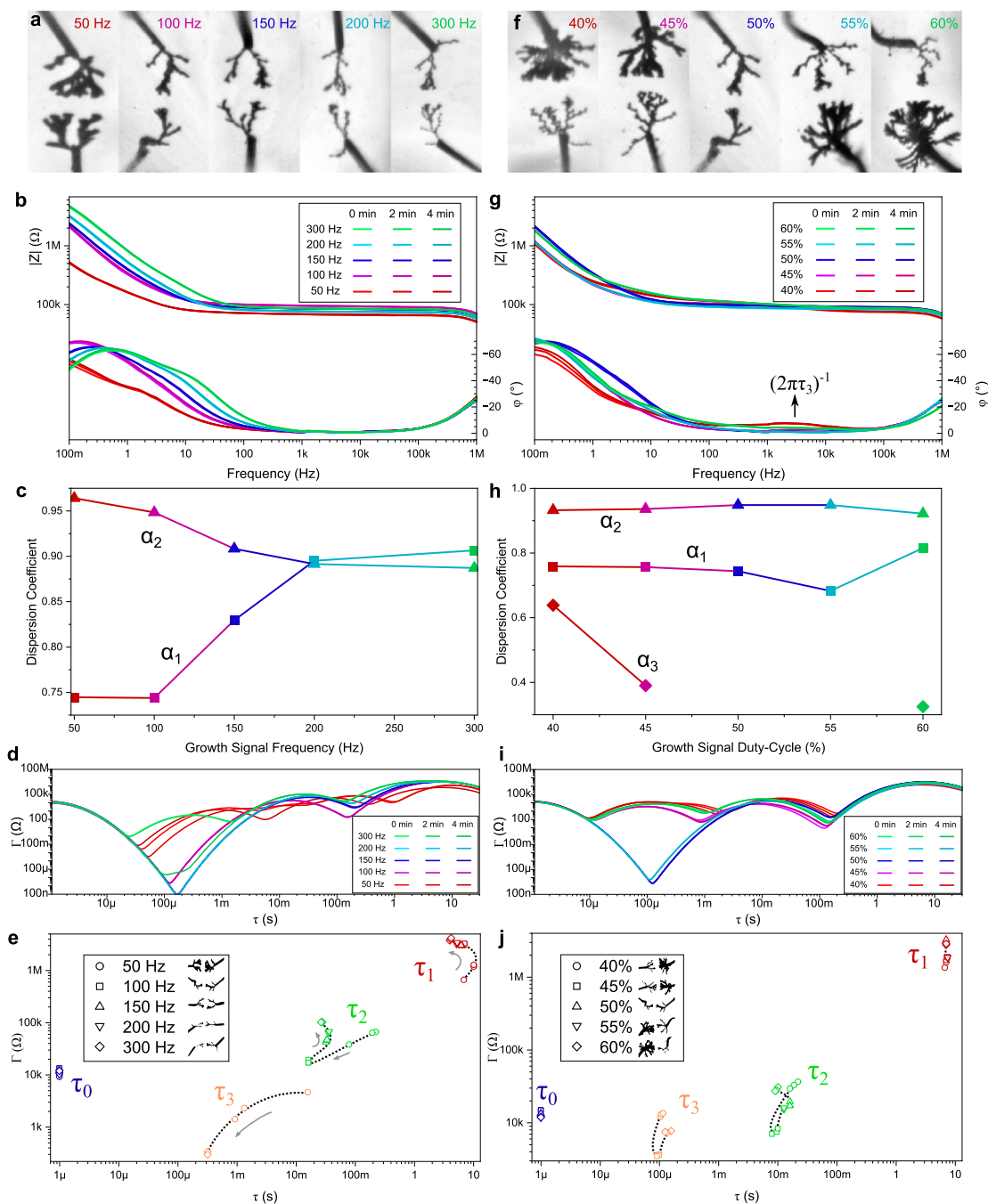


Fig 4. Different dendrites' morphologies and their respective impedance **a**, Pictures of the different morphologies obtained by varying the frequency of the square wave voltage. **b**, Bode plots of the corresponding dendrites, each impedance taken three times in a row to evaluate the stability over time. **c**, α_1 and α_2 extracted from the last impedance data of the series of three, for each dendrite. **d**, Corresponding DRT (including the series of three for each dendrite). **e**, Dependency of Fig. 4d's DRT local maxima of $\log(\gamma)$ with $\log(\tau)$. **f**, Pictures of the different morphologies obtained by varying the duty-cycle of the square wave voltage. **g**, Bode plots in magnitude and in phase for dendrites formed with different duty-cycles; again by sets of three measurements. **h**, α_1 , α_2 and α_3 extracted from the last impedance data of the series of three, for each dendrite. **i**, Corresponding DRT (including the series of three for each dendrite). **j**, Dependency of Fig. 4i's DRT local maxima of $\log(\gamma)$ with $\log(\tau)$.

the growth. A longer time for electropolymerization may lead to more accumulation of charged species within the bulk of the polymer, possibly leading to OMIEC with differences of conductivity either for the ions and/or for the holes. To verify that the relaxations are not specifically localized on one particular CPD compared to the other, dendrites are formed with different duty-cycle values on the pulse waveform used for their growth. Different polymerization times were required depending on the duty-cycle to reach comparable completion d/D , leading to a clear unbalance in their morphologies as shown in Fig. 4e. Branches that arise do not

only grow on the tip of the gold wire, but also on its edge, as an unbalance in polymerization times gives more time to electroactive oligomer particles to reach longer distances.⁷⁵ On the other hand, the electrode with shorter electropolymerization times shows thinner branches, with regularly spaced sharp angles. Both electrodes cover a larger area with multiple growth directions, which seem to follow the electric field lines. Five different values of duty-cycle (40%, 45%, 50%, 55%, 60%) were tested. Above 60%, bubbles started appearing at the work frequency, disturbing the impedance measurement. Electrolyte bubbling occurs because the duty cycle affects the

DC component of the periodic signal waveform. If the duty cycle deviates too much from 50%, it can push the DC component beyond the electrochemical window of the electrolyte solvent.⁶⁵ In their corresponding Bode plots in Fig. 4g, we can observe that the same effect of fluctuating electrolyte resistance $1/G$ exists at high frequencies, because also in this case, the number of branches is not easy to control with the growth. However, a discernible change in slope appears in the 1-10 kHz range, likely corresponding to the $R|CPE_3$ relaxation (pointing arrow in Fig. 4g). It is especially visible for duty-cycle values at 60% and 40%. While the high frequency plateau is usually flat and close to 0° in phase, in these specific extreme cases, the plateau appears to decrease in magnitude while the phase shows a slight bump above 0. This effect was not observed before. The appearance of $R|CPE_3$ in the raw data of the EIS is attributed to the growth under an asymmetric duty-cycle. Using $n = 3$ for Fig. 1e's model in these specific cases, similar values of α_1 and α_2 were obtained for all five samples in Fig. 4h. Only samples grown with duty-cycles of 40%, 45% and 60% show convergence of the $n=3$ model for their impedance fitting, leading to a value for α_3 . The fitted time constants of the circuit appear to follow a symmetrical trend with the duty-cycle: the time constant τ_2 gets longer as the system becomes more asymmetrical. Considering α_3 reaches a value below 0.5, it is unlikely that this $R|CPE_3$ relaxation should be modeled as a Voigt element, and a Randles element containing two constant phase elements could be physically more relevant here. In that case, the interpretation of the DRT could significantly change in Fig. 4i,j as the system would not be seen as a series of n Voigt elements anymore, making it not suitable if the diffusive term of the Randles element becomes dominant. We can however notice that if all relaxations follow Fig. 1e's model, we also observe a duty-cycle symmetry in Fig. 4j for τ_2 and τ_3 by the trajectory of their relaxation center (markers for 40% and 60% are closer to one another than to the other samples markers for these two relaxations).

Discussion.—The structural evolution of conducting materials gathers natural peculiarities when compared to conventional electronics in which no mass transfer occurs. Various transports and charging modes govern CPD, from nucleation to interconnection^{66,75,94}. Their electrochemical relaxations become slower as they grow, while resistance takes over reactance in the impedance. Some relaxations are slow at the timescale of seconds: often seen as a drawback in conventional electronics where computing speed is key^{95,96}, such fading memory in the charged state can be relevant for unconventional computation where recurrence is an important ingredient of the analog information processing^{97,98}. Multiple relaxations are simultaneously observed, but the most dominant is systematically the slowest one, followed by a second relaxation a few decades faster. Those two relaxations are heavily changed by the PEDOT:PSS deposition, starting from the very first milliseconds, but were already present without PEDOT:PSS in a context of gold wires immersed in a binary electrolyte (even without EDOT monomers). Considering this, the slowest relaxation can be attributed to a diffusive process taking place in the diffusive layer of the electric double layer of the wire, while the second relaxation is more consistent with the formation of the EDL, in terms of timescale, and as it was shown to be influenced by the evaporation of the solvent and EDOT monomers. When adding PEDOT:PSS on the wire, the surface area increases over time leading to a decrease of impedance over all timescales. It was observed that in the case of τ_1 , R_1 decreases substantially, while for τ_2 , R_2 increases, and it is both α_2 and Q_2 through the effective capacitance who are responsible for the decrease in impedance. The same cause (increased surface area) will offer different parameters responses (R_1 decreasing, R_2 increasing) because of the differing natures of the relaxations. The dynamics of charge storage is also slowed down while the diffusion is more constrained inside the polymer. The decrease in ideality can be explained by the porous nature of the CPD that can lead to a decrease of α_2 , and the 3D nature of the PEDOT:PSS coating when compared to the 2D surface of the gold wire. More relaxations are also evidenced, residual, but observable directly from the impedance raw data in some

cases. The coexistence of multiple relaxations in a simple two electrodes system relies on the complexity of the interface dictating the dynamics. For instance, the polaron coupling between holes and anions intricates the slow dynamics of an electrolyte with the multiscale structuration of electrically conducting dendrites^{71,99–102}. This may explain the dispersive character of the measured impedances when dendrites do not connect, however, at this stage, the physical origin of the equivalent electrical circuit model's parameters could not be formally evidenced. Despite new branches growing after the dendrites interconnected, their contribution in the system impedance is insignificant. Therefore, it appears necessary for a metamorphic electronics to operate in a regime where interconnectivity is only sparsely composed of completed dendrites to program the impedance between multiple nodes in a network. It is also noticed that the distance between the dendrites does not affect significantly the impedance of a junction, but a slower dynamics for the second relaxation is observed. This demonstrates the possibility to co-integrate multiple dendrites in a medium and to program the interconnectivity between them through their impedance, without their vicinity affecting the weight between specific interconnections. The relaxations' nature remains unclear: Nyquist plots do not feature Warburg elements with -45° straight lines, and the systematic observation of constant phase elements with $\alpha > 0.75$ suggests the absence of diffusion limitation in the charging/discharging process. In contrast to multiple studies reporting diffusion limitation with PEDOT:PSS thin-films^{103–107}, the topological nature of such an electropolymerized amorphous material is likely to condition the impedance of the electrochemical system, rather than the crystallinity of a colloidal phase of conducting domains percolating in an ion-conducting ionomer^{71,104}. Values of the dispersion coefficient α below 0.5 have also been observed: although they are not often seen experimentally with the exception of subdiffusion cases¹⁰⁸, they evidence important concerns on the nature of the charge transport through topological amorphous conductors. Various hypotheses can be proposed, such as the remain of polyelectrolyte excesses, trapped in the structure during the growth¹⁰⁹, or the difference in mobility of cations and polyanions in water's bulk¹¹⁰, through water channels inside the dendrite¹¹¹, or through the dendrite material itself as a compound with the PSS cation conductor¹¹². The symmetric DRT peaks suggest that the relaxations do not obey Gerischer's impedance underlying the Havriliak-Negami dispersion^{83,113}, but the possibility for multiple processes involving CPE and occurring in parallel should be considered. This can be explained by the existence of different ions or charged particles of various lengths having the same polarity but not the same permeation through a single dendrite morphology, and all occurring at a given time on the same dendritic electrode. As a possible way to verify these assumptions, a future characterization of these systems in the time domain shall be considered with different asymmetrical voltages to promote ion electrostatic attraction independently from diffusion with different morphologies of dendrites. The variation of their electrolyte environments under such stress shall also help decoupling the contributions of cations and anions, in addition to solvent properties which may play a key role in the signal transport, such as polarity, proton lability and viscosity.

Conclusions

In this study, we characterized electrogenerated PEDOT:PSS dendrites connecting two gold electrodes using EIS. An equivalent circuit model has been proposed based on the number of relaxations observed in the corresponding DRT. It has been shown that each observed relaxation has its own dependency to parameters such as the electrolyte composition and dendrites morphology. During their evolution, CPD go through three phases: the nucleation phase has a significant impact when the first monomers are electropolymerized, as a substantial drop in impedance magnitude occurs. The growth phase has an effect on the time constants of the primary relaxations which increase as more material is deposited and is branching out. Finally, at the connection phase, the conduction mode switches from mainly ionic to electronic, where most of the spectral features

associated to the dendrite morphologies are lost in the impedance. A correlation has been identified between the dendrites' morphology and their corresponding impedance: the time constants of this system can be changed by tuning the thickness of the dendrite's branches, but no specific link between individual parameters of each dendrite's constant phase elements and their morphology was established. By engraving the past-voltage history in their morphology, CPD interconnections are promising for future integration in unconventional computing devices, by storing electrically-accessible information with a low enthalpy process using carbon-based resources and additive manufacture. The perspective to implement it at the system level on a hardware classifier requires to verify the correspondence of the observed spectral features in the time domain. Future studies shall focus on programming such interconnects using spike voltage sequences in the time domain so as to observe the rich dynamics of these systems and the non-volatility of impedance modification through electropolymerization. This study paves the way for the implementation of recognition/classification tasks in future-emerging information-generation nodes embedding in *materio* computing resources, and is also a step toward evolvable electronics shaping its interconnectivity in operando using both its environment and mass transfer as a way to self-manufacture and process electrical information in a circuit.

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Competing interests

The authors declare no competing interests.

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