On the mechanism of the hysteresis and offset of current–voltage characteristics of diodes based on organic materials

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Abstract

Experimentally observed peculiar features, like hysteresis and offset of current–voltage (IV) characteristics, of Ag/copper phthalocyanine (CuPc)/ITO prototype devices are analyzed alternately in terms of bulk trapping of electronic charges, dielectric relaxation and reduction/oxidation (redox) reaction of mobile ionic species at the ITO electrode. Scanning the bias of the ITO electrode from reverse (negative) to forward voltages at rates corresponding to delays between successive current readings shorter than ≈ 10 s, the measured current passes through zero at significant negative potentials (offsets) before reaching zero potential. The current, however, is minimal close to zero potential when the scan direction is reversed. In order to elucidate the most probable mechanism of the offset, effects of several physical parameters have been considered: density of mobile ions or deep trap levels, delay time between two successive measurements separated by a potential step ΔV, bulk conductivity σ(T) of the organic material and temperature T. For both the charge capture/emission at traps and the dielectric relaxation involving the capacitance C_d of a depletion region, unrealistic trap (charged defect) concentrations are needed to comply with the experiment. Oxidation of the initially reduced (neutral) species, accompanied by an irreversible homogeneous chemical reaction of the reduced species, has also been considered. Still, two consecutive voltammetric cycles provided identical results, thereby making this option questionable. The most reliable non-conflicting interpretation is the charging of a double ionic layer capacitance at the CuPc/ITO interface through the high resistance of the "neutral" bulk of CuPc. The origin of the double layer is the protonation of CuPc as a consequence of the chemical treatment of ITO prior to CuPc deposition.

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1. Introduction

State-of-the-art microelectronic technology, based on inorganic substrates and active inorganic semiconductor layers, encounters physical limits imposed by the trend toward further miniaturization of the devices and integrated circuits. In parallel with this progress of microelectronics there is an increasing interest in opening new ways of producing low-cost alternative electronics, benefitting from either organic/inorganic or all-organic technology. One of the promising solutions is

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certainly large-area plastic electronics to be made compatible with a continuous rotary printing process rather than the lithographic fabrication [1]. Organic field-effect transistors (OFETs) [2,3] and light-emitting diodes (OLEDs) represent the objects deserving primary interest. The physics of the latter type of devices was thoroughly reviewed by Brütting et al. [4]. Apart from recent attempts to dope organic thin films either during or after the deposition [5], this new category of devices can be classified as one based on charge injection phenomena. Predominantly charge injection and recombination at metal–organic interfaces are considered [6]. Quite recently Baldo and Forrest [7] came to the conclusion that the injection is limited by charge hopping out of interfacial molecular sites whose energy distribution is being broadened by local disorder in an interfacial dipole field. Following the analysis presented by deMello et al. [8], the presence of mobile ions of whatever origin in active layers of OLEDs may have a crucial positive impact on the performance of the devices via making the electrode–organic contacts ohmic. Formation of an ionic space–charge region at the electrodes leads to a substantial lowering of the electric field in the bulk of the organic layer. Therefore, both the electron and hole currents are driven by diffusion rather than electro-migration of the electronic species. Irrespective of the specific mechanism of the transport of the electronic species, it is expected that eventual trapping of either electrons or holes at bulk and interfacial traps would deteriorate the performance of organic devices [9–11].

It is understandable that in the research field of OLEDs most of the effort has been focused on the optimization of forward current–voltage characteristics of single- or multi-layer devices. Looking at the OFETs, the ac impedance and transient behavior of the metal gate/organic interfaces under reverse biases may be of considerable interest from the point of view of wide-band and economic operation of the gate-driving circuitry. In addition, a stable threshold voltage and minimized power consumption in the off-state of electronic switches is mandatory for use, e.g., in mobile, battery-operated communication devices. High rectification ratios of $10^3–10^5$ were reported for organic diodes based on hole transporting materials: poly-(p-phenylene-vinylene) (PPV) [5], $N,N'-$diphenyl-$N,N'-$bis(1-naphtyl)-1,1-biphenyl-4,4-diamin (NPB) [12] and copper phthalocyanine (CuPc) [13]. ITO (indium-tin oxide) substrates have been exclusively used as the hole injecting anode under forward biases. It is quite common that the reverse current–voltage ($IV$) characteristics, monitored while scanning the bias in a cycle, exhibit not only a hysteresis but also a varying negative offset of the bias $V_{off}$ applied to ITO at which the reverse current goes through zero [5,10,12,13]. This observation is restricted to the bias half-scan starting at some negative bias and proceeding towards forward (positive) biases. The offset $V_{off}$ depends mainly on the bias scan rate $z = \Delta V/\Delta t$. Here, $\Delta V$ is the bias step (positive) on detuning the bias, $\Delta t$ is the delay time between two successive readings of the current $I$. Nguyen et al. [12] simulated the occurrence of the $IV$ offset in NPB-based diodes resulting from $\Delta V = 0.1 \text{ V}$ using the 2D device simulation program ATLAS and the assumption of charge capture and release at deep traps. Our present study is devoted to a critical reexamination of the possible origin of the offset, the analysis bearing against original experimental data obtained for $|V| \ll k_BT/q$ ($k_B$ – Boltzmann’s constant, $J$ $\text{ K}^{-1}$, $T$ – temperature $\text{ K}$, $q$ – electronic charge $\text{ C}$) on Ag/CuPc/ITO devices prepared and characterized in ultrahigh vacuum (UHV). Analytical formulae are provided for all the alternatively simulated mechanisms which can lead to an $IV$ offset.

2. Experiment

CuPc (of 99.996% purity) was purchased from SynTec GmbH, the ITO (100-nm thick) on glass substrates from PGO company were thoroughly cleaned in an ultrasonic bath in acetone and isopropanol for 30 min each, followed by boiling in the solvents for further 5 min. After drying the ITO surfaces in a nitrogen flux the substrates were transferred into an UHV chamber (base pressure $< 2 \times 10^{-10} \text{ mbar}$), where CuPc and Ag depositions took place. Approximately 220- and 300-nm thick layers of CuPc were deposited from a
Knudsen cell at a controlled deposition rate of about 1 nm/min. After the organic deposition Ag dots of three different sizes were deposited through a shadow mask onto the CuPc films. The largest size, corresponding to an area of $2.12 \times 10^{-3}$ cm$^2$, was used for the electrical in situ measurements.

$IV$ data were obtained using a Hewlett Packard pA-meter Model 4140B sweeping the bias typically from $-5$ to $+5$ V and back, the smallest step height $\Delta V$ available being 0.005 V. Both the measured and the computed $IV$ characteristics show the absolute value of the current as a function of the applied bias $V_{\text{ITO}}$. Our current sign convention assigns a negative sign to the steady-state reverse current at negative biases on ITO, while the forward current is taken as positive. The only exception is the gate voltage $V_{i}$ $(i = 1, 2)$ of the Ag electrode and the built-in voltage $V_{\text{bi}}$, both taken against ITO when modeling the response of traps.

To visualize the offset (current reversal bias $V_{\text{off}}$) of $IV$ characteristics of the CuPc-based diodes described qualitatively in Section 1, a set of representative measured $IV$ characteristics is plotted in Fig. 1. It is apparent from the figure that the negative shift of $V_{\text{off}}$ in the course of the starting half-cycle is enhanced by making the delay $\Delta t$ shorter. The $IV$ cycle started at an applied voltage of $V_{\text{ITO}} = -5$ V (potential of the ITO substrate versus the top Ag electrode). Returning to this starting potential from $V = +5$ V, there is essentially no remarkable offset of the minimum in the absolute current value $(V_{\text{off}} \approx V)$. Note that the amplitude of the step $\Delta V$ is much lower than $k_{B}T/q$ at ambient temperature $T$. Delays close to $\Delta t \approx 100$ s are needed to obtain the true steady-state $IV$ curve. In what follows we provide a review of possible sources of this spectacular behavior. In principle one deals with a competition between the steady-state current driven by the negative applied bias and a transient current of opposite direction (sign) initiated by each bias step $\Delta V > 0$. We followed this supposition when selecting appropriate mechanisms potentially leading to such a competition.

3. Models for the $IV$ offset

3.1. Trapping of electronic charges at deep trap levels

This section may be regarded as an excursion into the transient current response of deep localized states in the bandgap of a semiconductor, changing their steady-state occupancy in the rhythm of excitation. The kinetics of the current response plays a crucial role when assessing the amount of charge available. The delay of the observation time $\Delta t$ is involved in the simulation of the total released charge $Q_{b}$ as a function of the bias step amplitude $\Delta V$.

The electronic process of interest is confined to reverse biases where injection from either the ITO or Ag electrodes is negligible and thus no significant space-charge should build up in the organic layer. Actually, a rigorous treatment of the case of a hole-only transporting organic layer should not ignore the increased hole density at the injecting Ag electrode. Since in general the capture rate of holes at traps is proportional to the density of free charge carriers, it is not feasible to try a spatial profiling of the density of traps. On the other hand, in the case of an undoped semi-insulating layer one expects a Debye’s screening length exceeding the layer thickness $L$. Then we tend to view the organic layer as a fraction of the region.
depleted of free charge carriers. Even if there would be some significant energy band bending, from simple geometrical consideration it is possible to deduce that in the case of a linearized potential profile the corresponding width $\Delta x$ of the region, where the occupancy of traps has changed in response to $\Delta V$, is always larger than the corresponding width in the presence of band bending. Since the acquired concentration of traps is proportional to the inverse of $\Delta x$, the linear approximation of the potential through the organic layer leads to underestimating the trap density. In other words, if one is interested in the lower limit of the density and this is our case, a linear model of the potential through an insulating layer may be applicable, as was the case for amorphous Si:H-based thin film transistor-like (TFT) devices [14].

The model presented in Fig. 2 is compatible with the one found in the review article by Brütting et al. [4]. The layer of the width $L$ is equipped with contacts $M_1$ and $M_2$, respectively, the depicted situation corresponds to a positive built-in voltage $V_{bi}$ due to the electron work function of $M_1$ being lower than that of $M_2$. This does not necessarily correspond to the real Ag/ITO couple of contacts, as explained later. Transition from the originally positive bias $V_1$ to the reduced value $V_2$, which corresponds to a negative bias step $\Delta V = V_2 - V_1$ at the gate, is accompanied by the capture of holes at the bulk energy level $E_i$ positioned above the equilibrium Fermi level $E_F$ at flat bands. The capture of holes is spatially confined within the excited volume element of width $\Delta x = x_{c2} - x_{c1}$ and of unit area. This statement is a result of making an approximation and deserves an explanation. The change in occupancy is in fact demarcated by the equilibrium Fermi level crossing the trap level under reverse biases. Denoting the total voltage $V_i + V_{bi}$ as $V_{Ti}$, the potential $\phi(x_{ci})$ is

$$\phi(x_{ci}) = V_{Ti}(1 - x_{ci}/L).$$  \hspace{1cm} (1)

An inspection of Fig. 2 yields

$$E_i - E_{HOMO} = E_F - E_{HOMO} + q\phi(x_{ci}).$$  \hspace{1cm} (2)

Combining Eqs. (1) and (2), we obtain

$$x_{ci} = L[1 - (E_i - E_F)/qV_{Ti}].$$  \hspace{1cm} (3)

Evidently, the position of the crossover $x_{ci}$ of the trap level $E_i$ and the Fermi level $E_F$ at a selected bias $V_{Ti}$ is a function of the energy separation of the two at flat bands, rather than of the trap depth $E_i - E_{HOMO}$ related to the possible transport band for holes $E_{HOMO}$. Assuming a bulk trap density $N_i(x)$, an exact expression for the amount of the total released charge $Q_0$ should include the integral

$$Q_0 \propto \int_{0}^{L} N_i(x)[f_1(x, E_i) - f_2(x, E_i)] \, dx,$$

where the Fermi–Dirac statistics is taken for the occupancy of the trap at a particular bias $V_i$:

$$f_i(x, E_i) = \{1 + \exp[(q\phi_i(x) - E_i)/k_BT]\}^{-1}, \quad i = 1, 2.$$  \hspace{1cm} (5)

Nevertheless, when interested in a rough estimate of the quantity $Q_0$ and the related trap-limited transient current $i_T(\Delta t)$, for a small-signal excitation ($\Delta V \ll k_BT$) one can place the slowly varying $N_i(x)$ in front of the integral and the accuracy of the approximation of the integral $\int (f_1 - f_2) \, dx$ through $\Delta x$ is satisfactory. Adopting these abrupt changes in occupancy, we find two important features in the behavior of the crossover $x_{ci}$: first,
for any trap level located at the Fermi level ($E_i \approx E_F$) the crossover reaches the counter electrode $M_2$ second, there is no crossover at all at flat bands ($V_T = 0$).

Now we are going to tackle the issue of the kinetics of the transient current $i_T(t)$ due to the change in the equilibrium occupancy of the trap level. It is convenient to introduce a discrete time constant $\tau(T)$ defining the rate at which the charge $Q_0$ is captured or released from the traps:

$$Q(t) = Q_0[1 - \exp(-t/\tau)].$$

With regard to Eqs. (4) and (6) it may be obvious that the time dependence of the transient charge $Q(t)$ comes from the evolution in time of the fraction $N(t)/N_T$ of occupied traps $N(t)$. In fact we have to deal with the principle of detailed balance between capture and emission rates as signatures of the trap level [15]. Restricting ourselves on the excitation of the traps in dark and introducing the rates at which holes are either captured at ($e_p$) or emitted from the trap level ($e_p$), the kinetic equation reads [15]:

$$\frac{dN(t)}{dt} = e_p(N_T - N(t)) - c_pN(t).$$

One should consider two solutions:

(i) traps being initially filled ($N(0) = N_T$):

$$N(t) = \left(\frac{e_p}{e_p + c_p}\right)N_T + \left(\frac{c_p}{e_p + c_p}\right)N_T \times \exp\left[-(e_p + c_p)t\right],$$

(ii) traps being initially empty ($N(0) = 0$):

$$N(t) = \left(\frac{e_p}{e_p + c_p}\right)N_T\left[1 - \exp\left(-(e_p + c_p)t\right)\right].$$

In the absence of any space-charge the time constant $\tau = (e_p + c_p)^{-1}$ is the same for both charging and discharging the traps. The equilibrium occupancy is

$$N(\infty) = \left(\frac{e_p}{e_p + c_p}\right)N_T.$$

When deriving the desired expression for the transient current $i_T(t) = dQ(t)/dt$ from the excited volume $S\Delta x$ we take for simplicity $N(0) \approx N_T$, $N(\infty) \approx 0$ instead of $N_T/2$ to punctuate that we are interested in the lower limit for $N_T$, and $Q_0 = qSN_T\Delta x$, $S$ being the electrode area. Then according to Eq. (6) the current $i_T(t)$ takes the form

$$i_T(t) = \frac{qSN_T\Delta x}{\tau} \exp(-t/\tau).$$

When simulating $i_T(\Delta t)$ versus $V_{ITO}$ dependence (Fig. 3), we expressed the time constant simply as $\tau = \tau_0\exp(\Delta E/k_B T)$, taking $\Delta E = E_i - E_{HOMO}$. The figure is an illustration of the fundamental property of the transient current, peaking before reaching the cutoff at flat bands, i.e., at $V_{ITO} = V_B - (E_i - E_F)$, as shown earlier for the correlated transient charge (excess feedback charge capacitance) [14].

Since we are interested predominantly in the possible mechanisms causing the transient currents competing with the steady-state current, we can regard the latter as a constant reference used for all situations discussed. When expressing the steady-state reference current, we have chosen the well-known formula for the reverse thermionic current density of a Schottky diode [16] and adjusted the barrier height $\phi_B$, as to obtain the saturation current of about $10^{-12}$ A at $T = 300$ K:

![Fig. 3. Simulated trap-limited currents sampled at different delays $\Delta t$ after the bias step $\Delta V$, while scanning the applied bias $V_{ITO}$, are shown. The cutoffs correspond to flat bands, the time constant of the current decay is defined as $\tau = \tau_0\exp(\Delta E/k_B T)$.

\[
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\]
\[ J_i = \left[ A' T^3 \exp \left( -\frac{\phi_b}{k_B T} \right) \right] \left[ \exp \left( \frac{qV}{k_B T} \right) - 1 \right], \]
\[ A' = 8.16 \text{ A cm}^{-2} \text{ K}^{-2}. \]

Eq. (12)

It is just a reference, we do not pretend on this expression as the only possible mechanism of the reverse current flow. Actually, when passing to high reverse biases, the reverse currents in Fig. 1 do not show the saturation predicted for the thermionic model. Now we are ready to show the results of simulating the net current \( I = I_i(T) - J_n(T)S \), taking the steady-state reverse current at negative values of \( V \) with negative sign. The symbol \( \phi_b \) is used as the Schottky barrier height, being equal to 0.9 eV throughout the present report.

The behavior of the net current \( I(V, \Delta t) \) is illustrated in Fig. 4. One can draw the conclusion that the negative offset voltage \( V_{\text{off}} \) is remarkable for short delays \( \Delta t \). For the given parameters \( \tau_0 = 10^{-11} \) s and \( \Delta E = 0.6 \) eV we have a time constant \( \tau = 0.117 \) s so that the transient current contribution ceases after a delay \( \Delta t \approx 5\tau \). When adjusting the computational time constant \( \tau \) in compliance with experiment, it is not essential whether we modify \( \tau_0 \) or the trap depth \( \Delta E \), throughout the present (isothermal) study rather the parameter \( \tau_0 \) has been modified. Suppose the trapping mechanism should apply, then the trap depth \( \Delta E \) is a crucial parameter to be extracted from measurements at different temperatures.

Another crucial parameter for the positioning of \( V_{\text{off}} \) is the magnitude of the bias step \( \Delta V \) — cf. Fig. 5. The interval of bias steps considered for the simulation extends over the step magnitudes of 0.1 V used by Nguyen et al. [12] and \( \Delta V = 0.005 \) V relevant for the present experimental data. Now the computation corresponds to \( T = 300 \) K and \( \tau(300 \text{ K}) = 11.7 \) s.

The same value of \( \tau(300 \text{ K}) = 11.7 \) s applies also to the simulated IV characteristics displayed in Fig. 6. It may be evident that the observation of a significant offset after 10 s elapsed from the application of the step \( \Delta V = 0.005 \) V is connected with unreasonably high densities \( N_T > 10^{24} \text{ m}^{-3} \) of the traps. We suggest that this approach might be discarded when treating the present data related to CuPc. Having such high localized electron sites densities and thereby small distances between adjacent sites, the Schottky barrier would be narrow enough to ease direct tunneling of charges from the electrode to the transport band of CuPc, now the transport band for hopping being possibly represented by the trap level itself. Moreover, a significant deviation of the reverse IV characteristics from the observed ideal thermionic law is expected for such situations. The drawback of the
model comprising a discrete trapping level is clear, nevertheless the broader (in energy) the band of trap sites, the higher is the probability of observing injection- and/or hopping-limited currents through the defect insulator [7]. In addition, the small signal excitation is not capable of recharging traps from a wide energy interval.

3.2. Dielectric relaxation

One of the well-established properties of Schottky barriers at rectifying contacts to inorganic semiconductors, intentionally doped by a defined density \( N_A \) of shallow acceptors, is the capacitance of the barrier at reverse biases \( C_{d} = \varepsilon_0 \varepsilon_S w(V) \), the width of the depletion region being [16]

\[
w = \sqrt{\frac{2\varepsilon_0 \varepsilon_S (V_b - V - k_B T/q)}{q N_A}}.
\]

Normally, the voltage drop across the “neutral” bulk is ignored. Passing to intrinsic (undoped) organic semiconductors, there may be a sufficiently high concentration of intrinsic deep levels charged (ionized) at the temperature of observation. Then the electrical behavior of the barrier might be similar to that of Schottky barriers of intentionally doped organic semiconductors like PPV [5,9]. However, the role of the “neutral” bulk in charge relaxation phenomena can no longer be neglected in materials with relatively low mobilities of charge carriers. Actually, we have to consider the charging of the nonlinear capacitance \( C_d(V) \) through the series resistance of the bulk \( R_b(T, V) = \sigma(T)^{-1} [L - w(V)]/S \). As pointed out by Jonscher [17], this type of dielectric relaxation has a frequency dependence identical to that of an ideal Debye system. In the time domain, we express the related transient charge as

\[
Q_D(t) = Q_{D0} \left[ 1 - \exp \left( -\frac{t}{R_b C_d} \right) \right],
\]

\[
Q_{D0} = \sigma(T) \Delta V.
\]

Then the dielectric relaxation current flowing in response to the bias step \( \Delta V \) takes the form

\[
i_D(t) = \frac{Q_{D0}}{R_b C_d} \exp \left( -\frac{t}{R_b C_d} \right).
\]

Strictly speaking, the \( R_b C_d \) product is not remaining constant during the transient, thereby suggesting a more complicated equation for the kinetics of the transient current. Fortunately, under the small-signal excitation conditions it is justified to take the product as a constant. The temperature dependence of the time constant of the dielectric relaxation is dominated by the conductivity \( \sigma(T) \):

\[
\sigma(T) = \sigma_0 \exp \left( -\frac{(E_F - E_{HOMO})}{k_B T} \right).
\]

Here, we are dealing with the total current at reverse biases, the influence of the bulk resistance \( R_b \) on forward IV characteristics is explained in the paper by Brüttig et al. [5]. Retaining expression (12) and the constant parameters entering it, we simulated the net reverse current as \( I = i_D(\Delta t) - J_s S \), while varying the delay \( \Delta t \). A behavior qualitatively compatible with our experimental data on CuPc-based diodes is seen in Fig. 7, taking \( S = 2.12 \times 10^{-3} \) cm², the concentration of charged defects \( N_A \) of \( 10^{17} \) cm⁻³ and \( \Delta V = 0.1 \) V. The latter two parameters comply fairly with those used for the simulation of Nguyen et al. data [12]. For completeness Fig. 8 has been added, showing the result of simulating the effect of temperature on the net reverse current while taking the same value \( \sigma_0 = 2.5 \times 10^{-2} \) Ω⁻¹ m⁻¹ as before. The temperature interval for observing the shift of the offset \( V_{off} \)
is relatively narrow, which is due to the barrier height $\phi_b = 0.9$ eV determining the thermal activation of the steady-state reverse current $J_n$ that is expected to dominate at elevated temperatures. The vanishing of the offset for a given $\Delta t$ at elevated temperatures is accelerated by the time constant becoming shorter – see Eq. (16). Fig. 8 can also be perceived as a reminder of the need for stabilizing temperature if reproducible data on $V_{off}$ are demanded.

It is not justified to abandon definitely this optional interpretation of the offset, as long as no reliable experimental data for a set of temperatures is available. On the other hand, the need for relatively high densities $N_A$ of deep "dopants", explained in the previous section, emerges again since $C_d \propto N_A^{1/2}$.

### 3.3. Faradaic (diffusion-limited) current

The reported $IV$ methodology showing the competition of transient and steady-state currents can be regarded as cyclic voltammetry as well [18]. The latter proved to be an extremely sensitive electro-analytical technique capable of detecting trace amounts of mobile ionic impurities in solutions. Nevertheless, a new branch called solid-state voltammetry is rapidly developing, as documented, e.g., by Kulesza and Cox [19]. The formalism of cyclic voltammetry is based on the assumption that the mobile ionic species carrying the Faradaic current diffuse toward the working electrode and undergo a (reversible) heterogeneous redox reaction of the type $A^+ + nq \rightleftharpoons A$, connected with both charge ($n$ electrons) and mass transfer between the medium and the electrode. Normally one obtains a peak $i_{FP}$ of the voltammetric current each time passing the potential $V$ corresponding to the standard potential $V^0$ of the reaction, the potentials being taken against some reference (inert) electrode. The concentration $c^0$ in mol cm$^{-3}$ is related to the peak current (in A) by the Randles–Sevcik expression [18] (at 25 °C):

$$i_{FP} = 2.686 \times 10^5 n^{3/2} S c^0 D^{1/2} \pi^{1/2}.$$  (17)

The symbol $D$ in Eq. (17) stands for the diffusion coefficient (in cm$^2$ s$^{-1}$) of the mobile ionic species. The development of digitally controlled voltage ramp generators replacing the analog ones initiated a discussion about the difference between the cyclic (linear ramp) and the staircase voltammetry [20]. An example of a staircase voltammogram (Fig. 9) that may apply to the data assigned to an irreversible redox reaction is the subject of the next
Fig. 9. Simulated Faradaic current flowing in the course of a single voltammetric cycle comes from a heterogeneous oxidation reaction of the initially reduced ionic species A at the standard potential $V^0$, accompanied by a simultaneous chemical (homogeneous) reaction $A \rightarrow B$. The respective rate constants $k$ were assumed to be equal one to another (0.5).

chapter. We are testing this approach to comply with the closely related observations of the offset and its long-term evolution reported by Nüesch et al. [13].

4. Discussion

From what has been treated in the preceding chapters, several charge transfer mechanisms seem to apply qualitatively to the observation of the offset of $I/V$ curves at reverse biases – Fig. 1. Now it is time to highlight one of the alternatives that would avoid evident conflict with the changes of the $I/V$ behavior when changing the crucial parameters of the corresponding model.

It is not surprising that up to now most attention has been paid to the expected response of traps to the bias step $\Delta V$, keeping the notion of a purely electronic charge transport in hole transporting organics. Apart from the above-mentioned deficit of trapped holes at long times of observation while considering reasonable trap densities in connection with the experimental data, this issue deserves additional treatment. With reference to previous work [14] there is a maximum of the sensitivity when detecting the traps positioned around the equilibrium Fermi level. This was the reason for taking $E_t - E_F = 0.1$ eV when pointing to the charge deficit at delays $t$ of tens of seconds. Now let us concentrate on the small-signal excitation regime when $\Delta V \ll k_B T/q$ and thus only the traps at the crossover $x_c$ of the trap level and the Fermi level change their occupancy. Put in other words, there is a negligible deviation from the equilibrium occupancy of $e_p/(e_p + c_p) \approx 1/2$, implying $e_p \approx c_p$. Such reasoning leads to the principle of superposition of the amounts of transient charges detected on charging and discharging the traps. Moreover, the unique time constant $\tau = (e_p + c_p)^{-1}$ is suggestive of observing an excess negative transient current during the second half of the cycle ($\Delta V < 0$). The latter would shift the offset $V_{off}$ to forward (positive) biases, this seems to be the case reported for Ca/NPB/ITO diodes by Nguyen et al. [12]. Their observation of the offset at forward biases while reducing the forward bias was mediated by the turn-on voltage of about 2 V for injecting holes from ITO. Unfortunately, there is no shift from zero to positive biases of the turn-on voltage in our Ag/CuPc/ITO diodes to verify the suggestion in a wide interval of delays. Really, according to our UPS data the work functions of both Ag and ITO of the Ag/CuPc/ITO diodes were approximately the same (4.3 eV ± 0.02 eV), leading to the sharp onset of the forward current.

Keeping the condition of small-signal excitation, the dielectric relaxation outlined above is a hot candidate for being responsible for the hysteresis and offset of the $I/V$ characteristics. Once again we can apply the principle of the superposition of charges for both polarities of the bias step and consider a unique time constant of the current decay. Yet the limit imposed on the measurable contribution of the transient charge by the available density of charged traps $N_A$ is experienced again if looking at Fig. 7, the $I/V$ curves corresponding to the step $\Delta V = 0.1$ V. Since according to Eq. (14) the total charge on $C_d$ is proportional to $\Delta V$, an extrapolation of the simulated data towards $\Delta V = 0.005$ V, a step compatible with our experimental data, would lead to charge relaxation effects below the limit of detection.
The essence of the electrochemical approach sketched in the end of the previous chapter resides in the possibility of a redox process taking place at the working (ITO?) electrode potential close to the standard potential \( V^0 \) of the reaction. If dealing with electro-active species in a conducting liquid (supporting electrolyte present) interfaced with the working electrode, one can suppose the applied potential to drop across the thin diffusion layer in the vicinity of the electrode. For a reversible process one expects an equal peak current \( i_{fp} \) twice during a single cycle at approximately the same potential, the polarity of \( i_{fp} \) being reversed on return. This is unlikely the situation depicted in Fig. 1, so the concept of a reversible redox reaction may not apply. Therefore, as an alternative we suggest investigating an irreversible reaction of the type

\[
A \iff A^+ \\
B
\]

possibly taking place at the ITO electrode. For the sake of simplicity we considered both the rate constant \( k_{het} \) of the reversible reaction \( A \iff A^+ \) and \( k_{hom} \) of the homogeneous chemical reaction \( A \rightarrow B \) to be equal to 0.5. Taking \( z = 0.1 \text{ V s}^{-1} \) and \( E^0 = -0.5 \text{ V} \), we obtain the cyclic voltammogram corresponding to the oxidation of initially reduced species A, shown in Fig. 9. Due to the homogeneous chemical reaction producing inert species B there is only a small fraction of the transient charge after turning over at \( V = 1.5 \text{ V} \) and returning to the starting potential \( V = -1.5 \text{ V} \). This demonstration may have invoked the objection that the electrochemical treatment is not capable of explaining the observed shift of \( V_{off} \) with \( \varphi(\Delta t) \) – see Fig. 1. As a matter of fact the applied potential \( V \) is divided between the capacitance \( C_{diff} \) of the diffusion layer and the “neutral” volume of the medium, in a similar way as in the case of the dielectric relaxation treated above. As expected, \( V_{off} \) detected at higher negative potentials \( V_{ITO} \) in Fig. 1 corresponds to higher steady-state currents (ignored by the simulation procedures operating with the saturation current) and, therefore, to higher voltage drops across the equivalent bulk resistance \( R^b \) of the “neutral” medium. As long as there is no relevant data on the diffusion coefficient \( D \) of the unspecified species A, we are not able to provide a reliable lower limit of their concentration \( c^0 \) using Eq. (16) and \( I_{fp} \approx 10^{-12} \text{ A} \). What can be done is taking an average \( D \) value of \( 10^{-12} \text{ cm}^2/\text{s} \) from the interval of values reported by deMello et al. [8] for mobile ions in organicics. Then choosing \( n = 1, \alpha = 0.005 \text{ V/s} \) (\( \Delta t = 1 \text{ s} \)) and expressing the molar concentration \( c^0 \) by the help of Eq. (17), we arrive at \( c^0 = 2.5 \times 10^{-8} \text{ mol/cm}^3 \) to obey \( i_{fp} = 10^{-12} \text{ A} \). The net concentration of ions \( N_{ion} \) is obtained as a product of \( c^0 \) and Avogadro’s number \( (6.02 \times 10^{23} \text{ mol}^{-1}) \), yielding \( N_{ion} \approx 1.5 \times 10^{16} \text{ cm}^{-3} \). This is a realistic value well below the above-estimated concentrations of traps needed for explaining the offset and hysteresis of the \( IV \) curves at reverse biases. However, one has to check whether the irreversible redox reaction is present or not. This is easily done by having monitored two consecutive voltammetric cycles – see Fig. 10. In the case of the irreversible reaction there should be only a negligible contribution of the Faradaic current during the second cycle, the documented perfect reproducibility of the voltammogram on repeated cycling is in a clear contradiction with the hypothesis of the irreversible redox reaction.

Our hypothesis of the electrochemical origin of the offset voltage has been strongly supported by the impressive work on electrochemistry of either ITO itself or its interfaces with hole-only triphenylamine (TPD) and electron-only tris(8-hydroxyquinoline) (Alq3) published by Nüesch et al. [21,22].

![Fig. 10. Two consecutive voltammetric cycles of an Ag/CuPc/ITO diode point to the absence of an irreversible redox reaction analyzed in the text.](image-url)
There is a sound evidence for a double ionic surface layer on ITO consisting of adsorbed protons covered by their counterions, thereby forming an interface dipole. They have been able to estimate the thickness $L_e$ of the double layer to be less than $2\text{ nm}$. Being aware of the problem of defining a macroscopic dielectric constant for such a thin layer, we have tried to express its capacitance $C_e$ taking $\varepsilon \approx 10$, $L_e \approx 1\text{ nm}$, the capacitance $C_e$ amounting to $1.9 \times 10^{-8}\text{ F}$. Selecting $\Delta U = 0.005\text{ V}$, $\Delta t = 1\text{ s}$, $\tau = 1\text{ s}$, and applying an equation similar to Eq. (15), while replacing the capacitance of the depletion region $C_d$ by $C_e$, we have obtained $i(\Delta t) \approx 4.5 \times 10^{-12}\text{ A}$ in full correspondence with present experimental data. The corresponding equivalent bulk resistance $R_e \approx 10^7\text{ \Omega}$ is suggestive of CuPc specific conductivity $\sigma(300\text{ K})$ of about $10^{-9}\text{ (}\Omega \text{ m)}^{-1}$.

When trying to explain the behavior of saturated photovoltage of single as well as double layer organic devices on ITO substrates of different acido-basicity, Nüesch et al. [22] have observed that protons can move in the organics under influence of the applied electric field. From this point of view, even in the case of CuPc we expect proton-related deep acceptor-like defects (traps) to be present predominantly at the CuPc/ITO interface. It may be these acceptors acting like interface states, which play a crucial role when analyzing the mechanism of the forward current [7]. With respect to the chemical treatment of ITO substrates used for the present study, the hydrogen species (protons and hydroxyl ions) may have come from the dissociated isopropanol [22], applied for cleaning the ITO surface prior to CuPc deposition at ambient temperature. The adsorbed hydrogen species cannot be removed by depositing the organics on heated ITO substrates, according to Nüesch et al. [22] they persist up to at least $350\text{ ^\circ C}$.

5. Conclusions

Unrealistic densities of charged defects are demanded to explain the hysteresis and offset of current–voltage characteristics of the Ag/CuPc/ITO diodes while considering the capture/emission at traps or the dielectric relaxation connected with charging and discharging the depletion layer capacitance as possible sources of the detected amounts of charge. The redox process at ITO substrates, accompanied by a homogeneous chemical reaction of some mobile ionic species, has also been considered. Yet, the results of consecutive voltammetric cycles have not confirmed presence of an irreversible redox reaction. In solid-state voltammetry [19] even local ionic movements are expected to produce measurable transient charges. Long-range movements of the ionic species would require presence of charge compensating counterions, a situation analyzed by deMello et al. [8]. They have predicted rectifying behavior of such systems for concentrations of ions below $10^{19}\text{ cm}^{-3}$. We have not included the formation of ionic space charges at the electrodes in our list of possible mechanisms of the offset of IV characteristics. Instead the simple model of dielectric relaxation, extended to the case when the capacitance $C_e \gg C_i$ of the electrochemical double-layer is charged through the bulk resistance of the “neutral” organic material, succeeded in matching quantitatively with the experimentally observed amounts of relaxing charge. This phenomenon is well known as parasitic capacitive charging in voltammetry [18], mainly in electrochemical cells without any supporting electrolyte. As to the origin of the ionic double layer, we appeal to the conclusion provided by the topical studies by Nüesch et al. [21,22] on the relation between acido-basicity of the ITO surface and the behavior of both IV curves and saturated photovoltage of organic-based devices. Protons and hydroxyl ions building the double layer of Ag/CuPc/ITO diodes are likely produced by dissociation of isopropanol used for cleaning the substrate, rather than by dissociation of water.

In final conclusion, there is an increasing interest in electrochemistry of the ITO/CuPc interface, already documented mainly by Nüesch et al. [13,21,22]. Experimental data on diffusivity of the ionic species are needed to improve our understanding of the long-term stability of organic layers intended for future applications. Nevertheless, there are definitely organic based systems showing trap-limited hysteresis phenomena at reverse biases, most probably carrying valuable information about the traps in the vicinity of the Fermi level. In such cases the temperature-dependent data on the
correctly extracted time constants may help to assess the position of the Fermi level with respect to the transport band of the material involved.

References