Dynamics in Electrochromic Windows Interpreted with an Extended Logistic Model

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Full-color electrochromic windows are based on tungsten oxide layers (WO₃) that change their color due to the intercalation of ions. Electrochemical intercalation is a complex process and several models have been proposed to describe it. One of these models is the Butler-Volmer equation, which describes the kinetics of electrochemical reactions at the electrode-electrolyte interface.

The approaches/models listed above can describe electro intercalation into WO₃ materials like WO₃. Early studies focused on approaches/models have been proposed to investigate electrochemical reactions in WO₃ resulting in the formation of so-called tungsten bronzes. Numerous approaches and models have been proposed to investigate electro intercalation into EC materials like WO₃. Early studies focused on the bleaching and coloring of WO₃ electrodes immersed in various liquid electrolytes. The time dependence of the coloration of amorphous WO₃ at low voltages was described in terms of a barrier for current at the WO₃-electrolyte interface. The coloring and bleaching processes of LiₓWO₃ films were examined in short time ranges considering diffusion-limited processes.

Extended Logistic Model

An EC window contains typically tungsten oxide layer (WO₃) as the primary EC material, which changes its color due to the potential-induced intercalation of protons or alkali ions into the WO₃ electrode resulting in the formation of so-called tungsten bronzes. Numerous approaches and models have been proposed to investigate electro intercalation into EC materials like WO₃. Early studies focused on the bleaching and coloring of WO₃ electrodes immersed in various liquid electrolytes. The time dependence of the coloration of amorphous WO₃ at low voltages was described in terms of a barrier for current at the WO₃-electrolyte interface. The coloring and bleaching processes of LiₓWO₃ films were examined in short time ranges considering diffusion-limited processes.

One has to bear in mind that the dynamics in complete EC devices (windows) can deviate from idealized models because of potential drops in transparent electrodes, contributions from other interfaces, non-stoichiometry of WO₃, as well as side reactions that may occur in real EC devices. Consequently, the classical diffusion-limited analysis of the electrochemical intercalation of species into a single EC electrode fails to reproduce the dynamics of the complete EC device, so that the fitting of experimental curves results in high deviations and the time domain should be reduced to a few tens of seconds.

In 1999, the so-called quadratic logistic differential equation was introduced by Torresi et al. for the interpretation of electrointercalation processes in electroactive films in analogy to the power response of a fuel cell described by Gonzalez. Using cyclic voltammetry data, it was proposed that the highly non-linear nature of the EC process can be described by a quadratic logistic equation (Equation 1) that is simple model for the density of a population that grows almost exponentially for small initial density and saturates at x = 1. The logistic model has been confirmed and elaborated later but also disputed by Sadkowski, who stated that the logistic equations are rather limiting forms valid in the special case of linear potential scan of a fully (ir-)reversible process.

This paper presents an extended logistic model based on the ligand and binding reactions described by the Hill’s model. It is a simple closed-form expression with four parameter that reliably fit experimental data and obtain useful device characteristics. The proposed approach is then a suitable approximation where its parameters might not have direct physico-chemical meaning but they can be easily interpreted in terms of the dynamics of a population growth. Even if the model does not consider detailed EC design, voltage drops across transparent conducting electrodes and electrolyte, etc. – one observes a remarkable agreement between the experimental and the simulated data. Importantly, the agreement is preserved in a wide range of potential and time (up to 50 min) once the total inserted charge is split in two components: one corresponding to the adsorption process following the diffusion growth and the second being accounted for diffusion-limited processes.

The paper is structured as follows. In section Quadratic logistic model the existing quadratic logistic model is reviewed. In section Extended logistic model the extended logistic model for the growth of tungsten bronzes is derived, starting from the consideration of the Langmuir isotherms, cooperative binding described by the Hill’s model and finishing with the analytic expression that describes the temporal evolution of population (or saturation level). Section Experimental setup and methodology provides details about experimental set-up and methodology of opto-electrical measurements of EC complete devices. Results are presented and discussed in section Results.
and discussion. First, the logistic model is applied to fit an experi-
mental chronocoulomonogram during a coloration transition and validated
for various bias voltages. Next, two commercial EC windows are
characterized, and their coloration dynamics is compared in terms of
four parameters of the logistic growth model. Finally, it is shown
how the evolution of the coloration efficiency can be understood and
forecasted on the basis of the extended logistic model.

Theoretical Background

Quadratic logistic model.—An electrochemical generator like a
battery or a fuel cell was proposed to be described by a quadratic
logistic differential equation.21 The energy flow $dx/dt$ is correlated to the energy (or voltage) $x$ according to

$$\frac{dx}{dt} = ax (1 - x) [1]$$

where parameter $a$ is the intrinsic growth rate. In this way the interpretation of the dynamical behavior of the system can be done with the general concept of dissipation, nonlinearity and feedback. The logistic differential equation was applied to interpret intercalation processes in electroactive inorganic and organic films like nickel hydroxide, tungsten oxide, polyaniline and polypyrrole modified electrodes.20 The logistic model was theoretically derived later by Diard et al.22 assuming Langmuir isotherm conditions, kinetic reversibility, uniform concentration in the films and a linear potential sweep. The differential equation 1 was therefore re-written as

$$\frac{d\theta}{dt} = f v \theta(1 - \theta) [2]$$

where $v$ refers to the sweep rate, $f = F/RT$ ($F$ is the Faraday constant, $R$ the gas constant and $T$ the absolute temperature) and $\theta$ is the intercalation level defined as

$$\theta = \frac{Q(t)}{Q_{\text{max}}} [3]$$

where $Q(t)$ is the charge density at time $t$ and $Q_{\text{max}}$ is the total charge density required for the saturation of the electroactive film. The above Equation 2 cannot be considered as a general relationship for intercalation processes and two possible deviations from the simple quadratic logistic equation were pointed out in Ref. 22: reaction kinetics and isotherm type.

On the other, it was recalled in Ref. 25 that particularities such as bifurcation, period doubling and chaos are manifested only in the dynamics of discrete systems, and the logistic equation is 2 valid only in the special case of linear potential scan and fully reversible (or irreversible) process conforming to the Langmuir isotherm, meaningful only for $\theta \in (0, 1)$, where its close form solution (trajectory) follows the relationship:

$$\theta(t) = \frac{1}{1 + \frac{1}{\theta_0} \exp(-f v t)} [4]$$

where $\theta_0$ is the initial state. The symmetric nature (parabolic-shape) of the power-voltage relationship in electrochemical power sources with constant internal resistances and its parallelism to the logistic differential equation was also discussed,25 but similarities between the particular forms of the logistic equations and electrochemical adsorption and intercalation processes were concluded to be fortuitous and valid for specific conditions (reversible or irreversible process at constant and positive potential sweeps).

Extended logistic model.—The Langmuir isotherm assumes no interactions between the absorbed species on the electrode surface.27 In this work we propose to extend the Langmuir isotherm in order to account for the cooperative binding of ligands, so that a second ligand $L$ can have more (or less) affinity for the receptor $R$ than the first one, and binding at one site can influence the binding at the others:

$$R + L \leftrightarrow RL + L \leftrightarrow RL_2 + L \leftrightarrow \ldots \leftrightarrow RL_n [5]$$

Such cooperative binding can be described by the Hill’s model26 to account for the sigmoidal growth of the saturation level $\theta$:

$$\theta = \frac{1}{1 + \left(\frac{1}{\theta_{\text{eff}}} \cdot \pi \right)^n} [6]$$

where $n$ is the Hill’s coefficient that it is related to the number of cooperative bounds and $K_{\text{eff}} = k_1 \cdot k_2 \cdot \ldots \cdot k_n$ is the dissociation constant that serves as a measure for the affinity of the ligand to the receptor: smaller $K_{\text{eff}}$ corresponds to a greater affinity. Malmstrom pointed out that the cooperative ligand binding approach can also be applied to electrochemical reactions, which in case of the EC process can be represented as:

$$WO_3 + z(M^+ + e^-) \leftrightarrow M_n WO_3 [7]$$

where the solid metal oxide $WO_3$ requires injection of charge $e^-$ and counter ions $M^+$ enter the solid. The composition of the reaction product is $M_n WO_3$, where $z$ depends on the charge passed and hence on the extent of electrode reaction. The quantity $z$ is termed the isenion coefficient and for tungsten trioxide $z$ typically increases from 0 to its maximum value $z_{\text{max}} = 0.4 \sim 0.5$ for the fully colored state.28 In this case the saturation level $\theta$ can be defined as:

$$\theta(t) = \frac{z(t)}{z_{\text{max}}} = \frac{Q(t)}{Q_{\text{max}}} [8]$$

The absorption of alkali ions by the porous $WO_3$ electrode through which they can diffuse and react chemically can be regarded as a kinetic process, where the reaction rate depends on the rate of supply of the ion species by diffusion. In our derivation we assume that diffusion of the active species is the only mode of mass transport and it governs the rate of the whole insertion process, whereas the electrode/electrolyte double-layer capacitance effects are neglected. Therefore, considering the Fick’s linear equation under the semi-infinite approximation, the diffusion can be evaluated according to the Cottrell equation:29

$$j(t) = \frac{Q_{\text{max}} D^{1/2}}{l^{1/2}} t^{-1/2} [9]$$

where $j(t)$ is the current density as a function of time, $Q_{\text{max}}$ is the total charge density transferred during the electrochemical alkali ion intercalation, $D$ is the apparent diffusivity, $l$ is the thickness of the electrode film and $t$ is the elapsed time. The surface concentration of ligands $\Gamma$ at time $t$ can be obtained from the current integration over time

$$\Gamma = K_{\text{eff}} [M^+] = \int_0^t j(t) dt [10]$$

resulting in

$$\Gamma = \frac{2Q_{\text{max}} D^{1/2}}{l^{1/2}} t^{1/2} [11]$$

By inserting Equation 11 into Equation 6 we propose a simple analytic equation to approximate the diffusion-limited adsorption process:

$$\theta(t) = \frac{1}{1 + \left(\frac{1}{\theta_{\text{eff}}} \cdot \tau \cdot \pi \right)^{n/2}} [12]$$

where $\tau = l^{1/2}/2Q_{\text{max}} D^{1/2}$ is a time constant and $\beta$ is related to the cooperative index from the Hill’s model as $\beta = n/2$.

Equation 12 can be re-written as a differential logistic function:

$$\frac{d\theta}{dt} = \beta \theta (1 - \theta) [13]$$

where $\beta$ is the growth rate per capita and here is interpreted in terms of the number of cooperative bounds. Please note that Equation 13 is formally equivalent to Equations 1 and 2, but with a time re-scale by
logarithmic transformation. The relative growth rate of the quadratic logistic function 13 declines linearly with increasing the population size and is given by the term \((1 - \theta)\), which yields symmetrical (parabolic) shape of the power-voltage relationship in electrochemical systems. In this study we would like to introduce an additional parameter \(\gamma\) in order to account for the asymmetry in the logistic function, claiming that the trap rate is proportional to \(1/\gamma\) power of the intercalation level \(\theta\):

\[
\frac{d\theta}{dt} = \beta \gamma \theta (1 - \theta^{1/\gamma}) \quad [14]
\]

Parameter \(\gamma\) does not have a direct electrochemical meaning but should account for non-ideal situations, additional interfaces, possible heterogeneity, etc. to empirically fit the electrointercalation process in EC windows. Unlike the asymmetry function introduced in Ref. 22, the characteristic shape of \(\gamma\) does not have a direct electrochemical meaning but should account for non-ideal situations, additional interfaces, possible heterogeneity, etc. to empirically fit the electrointercalation process in EC windows. 

Experimental Setup and Methodology

The proposed logistic model is validated on two different commercial EC windows. The active electrochromic layers in both devices are based on \(WO_3\). Device A has a solid electrolyte and is supplied as an insulated glass unit (IGU) in size 35.6 × 35.6 cm², whereas device B has a polymer electrolyte and it is supplied in size 40 × 40 cm².

The electro-optical characterization test-bench for EC IGUs is an automatic computer controlled system. It consists of a monochromator (model MSH300) and a halogen lamp as light source. The illumination is modulated by a chopper at a frequency of 300 Hz, where an optical fiber guides the monochromatic light onto the sample. An optical collimator is coupled to the fiber to increase the collection of incident photons and reduce the signal-noise ratio. A reference photodiode is placed on another side of the sample holder to measure the window’s transmittance, and it is electrically connected to a transimpedance amplifier that serves as a current-voltage converter. A synchronous amplifier (model SR830) measures the characteristic currents of such a low level of monochromatic illumination. 

The measurements are performed in a four terminal configuration by using a source-meter (Keithley 2450) that is set to a desired voltage and records the flowing current.

Results and Discussion

Chronocoulogram.—In the chronoamperometry technique, the electrode potential is abruptly changed from E1 to E2 and the resulting current variation is recorded as a function of time. The proposed logistic model will be evaluated through the obtained charge density by integrating current over time. The advantage of using this technique is that, based on the assumption that the electro-intercalation is diffusion-controlled and proportional to \(t^{1/2}\), the total charge can be split into two components:

\[
Q = Q_{ads} + Q_{diff} \quad [17]
\]

where the adsorbed component \(Q_{ads}\) is described by Equation 16 whereas the diffusion component \(Q_{diff}\) is expressed by the Cottrell equation \(Q_{diff} = 2nFD^{1/2}C^0\pi^{-1/2}t^{1/2}\).

A typical Anson plot30 for EC device A at a bias voltage of 0.1 V is shown in Figure 2. The contribution of the linear diffusion mechanism is determined from the linear fit \(Q\) vs. \(t^{1/2}\). A correlation coefficient higher than \(r^2 > 0.999\) is used to determine the linear range. The intercept gives the maximum charge hosted by the adsorption process \(Q_{ads,max}\) (the maximum value corresponding to \(\theta = 1\)). The contribution from the adsorption process is directly taken by subtracting the diffuse component \(Q_{diff}\) from the experimental result \(Q_{exp}\).

By normalizing to the saturation level \(Q_{ads,max}\), the evolution of the adsorption level \(\theta\) over time is displayed in Figure 3 for the same device A at 0.1 V. The dash-dot line represent the fit \(\theta_{fit}\) according to

\[
\theta \approx \frac{1}{1 + \left(\frac{t}{\tau}\right)^{1/\gamma}} \quad [15]
\]

where the population at the inflection point (where the growth rate is maximum) is \(\theta_{inf} = \left(1 + \frac{1}{\gamma}\right)^{1/\gamma}\) and it is reached at time \(t_{inf} \approx \tau(1/\gamma)^{-1/\beta}\). Please note that \(\gamma = 1\) reduces Equation 14 to Equation 13 and \(\theta_{inf}\) becomes \(\theta_{inf} = 1/2\). \(\gamma \gg 1\) describes an exponential growth and \(\gamma = 0\) determines the extreme \(\theta_{inf} = 1\). Confining parameters to positive values, we suggest to interpret the dynamics of electrointercalation processes in EC windows in terms of an extended logistic model with four free parameters of the form

\[
Q = Q_{max} \left[1 + \left(\frac{t}{\tau}\right)^{\gamma}\right]^{-\beta} \quad [16]
\]

Please note that the basic principles discussed in this text might also apply to different devices as electroanalytical sensors, batteries or fuel cells. Nevertheless, the main emphasis here is on the application of the method to the study of electrochromic windows, where possible correlations with the device structure and its material properties require further studies and developments which are out of the scope of the present work. The logistic model shows a remarkable potential to be widely used for quantitative analysis and interpretation of electrochemical systems in term of population dynamics. The effect of its four parameters on the shape of the logistic growth curve is displayed in Figure 1.

![Figure 1](image1.png)

**Figure 1.** Effect of parameters \(Q_{max}\), \(\beta\), \(\tau\) and \(\gamma\) in the logistic function (Eq. 17).

![Figure 2](image2.png)

**Figure 2.** Experimental chronocoulometry: charge vs (time)^{1/2}. \(Q_{exp}\), Determination of the linear diffusion \(Q_{diff}\) and adsorption \(Q_{ads}\) processes.
Equation 15, and the dotted line stands for the relative error defined as

$$\varepsilon (%) = \frac{\theta - \theta_{fit}}{\theta} \times 100\% \tag{18}$$

Although the error in the initial moments of the coloration process is high, it is quickly reduced as one approaches the saturation level.

**Voltage dependence.**—This section aims to describe and analyze the bias voltage dependence of the coloration process in terms of the proposed logistic model. Figure 4 illustrates the shape of the chronocoulogram and transmittance measurement of device A registered at applied potentials from 0.1 V to 2.0 V. Each applied voltage was kept for at least 30 minutes, and between each measurement the device was short-circuited for similar time to completely bleach and reset it into its equilibrium state, with very low or no stored charge. Please note that the inserted charge density is plotted in logarithmic scale for better visibility.

Two main effects of the applied potentials can be deduced from the charge evolution over time. First, the saturation level of the transferred charge density is considerably affected by the bias voltage. The second characteristic property is that its rate of rise during the first few minutes is similar for all bias voltages and it can be characterized by a linear characteristic property is that its rate of rise during the first few minutes is high, it is quickly reduced as one approaches the saturation level.

Figure 4 displays the inserted charge density and fits to the logistic model at bias voltages from 0.1 V to 1.0 V for device A (top) and from 0.2 V to 0.8 V for device B (bottom). The specific values of the applied potentials are irrelevant and intended to verify the validity of the model in a wide range of time and voltage. The model fit shows some slight deviations (which is specially highlighted in log-log plots) from the experimental behavior during the first ten seconds, when the transferred charge density is low. Afterwards, the electrochemical intercalation process is well described in a wide voltage range.

The voltage dependence of the model parameters $\tau$, $\beta$, and $\gamma$ for devices A and B are shown in Figure 6. The time constant $\tau$ related to the apparent diffusivity and device features (electrode thickness $l$ and transferred charge density $Q_{max}$), increase linearly with the voltage in device A but remains almost constant in device B. We do not observe a significant voltage dependence in device B. However, it remains almost constant in device B. Please note that interaction coefficients $4 < n = 2\beta < 6$ represent an average number of binding events in a sequential reaction and it should not be confused with the ligand ion (H$^+$ or Li$^+$) to W atom ratio which should be below $z < 0.5$ for electrochromism to occur in WO$_3$.$^{18}$ Finally, the asymmetry factor $\gamma$ in device B increase linearly, but no clear tendency is observed in device A.

The results of the quantitative analysis of the adsorption process is depicted in Figure 7, where voltage dependence of $Q_{ads,max}$ and...
θ_{dif}/I_{dif} is displayed. The maximum adsorbed charge in devices A and B increase linearly with the voltage and the tendency suggests that at higher potential device A absorbs higher charge density than device B. The rate of the maximum intercalation level in devices A and B decreases linearly with the applied voltage, being much faster device B than A at low voltages. In this voltage range device B also allocates higher charge density. However, similar intercalation rates are observed at higher potentials when the maximum adsorbed charge is similar.

Coloration efficiency.—The coloration efficiency (η) for an EC device is a measure of change in the optical density (ΔOD) induced by the transferred charge density (Q), which according to Ref. 31 can be calculated as

\[ \eta = \frac{\Delta \text{OD}}{Q} = \frac{\log \left( \frac{T_b}{T_c} \right)}{\int_0^\infty j(t) \, dt} \]  \[ \text{[19]} \]

where j is the current density, t_e is the elapsed time in the color transition and T_b and T_c are the photopic transmittance in the bleached and colored state defined as

\[ T_{b,c} = \frac{\int_{\lambda_{min}}^{\lambda_{max}} T_{b,c}(\lambda) I_p(\lambda) \, d\lambda}{\int_{\lambda_{min}}^{\lambda_{max}} I_p(\lambda) \, d\lambda} \]  \[ \text{[20]} \]

where \( \lambda_{min} = 400 \text{ nm}, \lambda_{max} = 730 \text{ nm}, \) \( T_{b,c}(\lambda) \) is the spectral transmittance in the bleached or color state and \( I_p(\lambda) \) is the photopic intensity function.

The trend for the coloration efficiency as a function of cycle number can be useful to evaluate performance losses. Obviously, a higher coloration efficiency means a better performance. The difficulty in using this parameter in the characterization and/or comparison of different EC samples lies in the highly non-linear dynamics of ion insertion (and therefore charge density) into the WO_3 electrode. This process introduces an additional difficulty to establish a time frame for determining a representative value of η. Figure 8 depicts the evolution of the experimental color efficiency (η_{exp}) and the optical transmittance of 650 nm (T_{650}) over time. The drop in the coloration efficiency in the final stage of the measurement is associated with the saturation of the adsorption process and the charge insertion due to the diffusion process η_{dif}. A clear non-linear behavior is observed for η_{exp}, where a maximum is reached shortly before the full color transition. The EC device is still dissipating current while the color state of the EC device remains almost constant.

We suggest that in terms of the logistic model the maximum coloration efficiency can be determined as

\[ \eta_{max} \approx \frac{\log(1/\varepsilon)}{T_b} \frac{dT}{dQ_{dif}} \bigg|_{t=t_{max}} \]  \[ \text{[21]} \]

where \( T_b \) corresponds to the transmittance in the bleached state and \( (dT/dQ_{dif})_{t=t_{max}} \) can be experimentally obtained from a plot \( T \) vs. \( Q_{dif} \). The suggested definition of the maximum coloration efficiency assumes that the adsorption of alkali ions has already reached the saturation level and the adsorption contribution to the coloration dynamics can actually be neglected.

Conclusions

An empirical model based on the logistic growth of colored tungsten bronzes in an electrochromic material is proposed. The logistic curve is derived in terms of the Hill’s model to describe cooperative electrowhitecoloration of the alkali ions into the WO_3 electrode. Its four main parameters are the charge saturation level \( Q_{ads,max} \), cooperative binding parameter (β), time constant (τ) and asymmetry factor (η). The proposed model has been validated on two commercial EC windows during the full color transition. Their chronocoulomgrams exhibit a strong voltage dependence that is experimentally characterized and discussed, although the correlation with the EC device structure and its material properties require further investigations. The logistic model of the ion insertion dynamics has a potential to be widely used for the quantitative comparison of complete EC devices by fitting experimental chronocoulomgrams.

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