Inductive Loop in the Impedance Response of Perovskite Solar Cells Explained by Surface Polarization Model

Elnaz Ghahremanirad,‡ Agustín Bou,‡ Saeed Olyaee,‡ and Juan Bisquert§,†,§

‡Institute of Advanced Materials (INAM), Universitat Jaume I, 12006 Castelló, Spain
§Nano-photonics and Optoelectronics Research Laboratory (NORLab), Shahid Rajaee Teacher Training University, 16788-15811 Lavizan, Tehran, Iran
§Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia

ABSTRACT: The analysis of perovskite solar cells by impedance spectroscopy has provided a rich variety of behaviors that demand adequate interpretation. Two main features have been reported: First, different impedance spectral arcs vary in combination; second, inductive loops and negative capacitance characteristics appear as an intrinsic property of the current configuration of perovskite solar cells. Here we adopt a previously developed surface polarization model based on the assumption of large electric and ionic charge accumulation at the external contact interface. Just from the equations of the model, the impedance spectroscopy response is calculated and explains the mentioned general features. The inductance element in the equivalent circuit is the result of the delay of the surface voltage and depends on the kinetic relaxation time. The model is therefore able to quantitatively describe exotic features of the perovskite solar cell and provides insight into the operation mechanisms of the device.

Perovskite solar cells have rapidly improved by an accurate design and engineering of the configuration of the active layer, electron and hole transport layers, and the interfaces. Many researchers have enhanced the morphology and crystallinity of the perovskite solar cells, making them a promising candidate for commercial use. Investigating and understanding the physical processes in the bulk and the interfacial layers are important topics in perovskite solar cells for the control of the device quality and for the design of new applications. Impedance spectroscopy (IS) is a useful tool to characterize physical processes in solar cell devices, and it has been applied extensively in the perovskite solar cells. Most of the early reports presented the suggestion of equivalent circuits, the comparison with previous hybrid solar cell systems, and the analysis of the resulting processes. Very interesting and unique behaviors that have been shown in the literature are the negative capacitance and also an inductive loop in the complex impedance plot. The negative capacitance at low frequency is a familiar feature on hybrid organic–inorganic solar cells, but explaining the specific microscopic origin of such feature is traditionally rather challenging. An inductive loop is a middle-frequency range feature that in some cases goes to the negative capacitance as well. This loop has been well established in perovskite solar cells, but the origin and significance of this loop for the solar cell operation is not clear at all. The inductance simply appears as a necessary feature in the equivalent circuits to fit the experimental data without a clear explanation of the physical process that creates it.

We provide an understanding of the origin of the frequently observed impedance loops based on a recently proposed surface polarization model (SPM) and without further assumptions. We also show the adequate description of experimental IS data by this model that is simply computed from the previously proposed equations, thus providing support to the model and additional insight into the kinetic properties of the perovskite solar cell.

Summary of the Surface Polarization Model. The SPM starts from the assumption that the formation of a voltage in a perovskite solar cell implies the accumulation of charge at the TiO2 electron-selective contact, as indicated in Figure 1. This observation arises from experimental results, which determined an accumulation capacitance that increases when the light intensity is incremented as well as the detection of surface charge in the perovskite layer. The band-bending structure at forward bias voltage in Figure 1 is established from detailed simulations. As before, V is the external voltage at the contacts and Vf is an internal surface polarization voltage associated with the accumulation layer of holes assisted by positive ion charge that results from the ionic displacement and compensated by electrons in the contact layer side of the interface. The excess charge density of holes at the interface is

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where $m = \gamma \beta / (\gamma + \beta)$. To complete the SPM in a transient situation the extracted current is composed by the photocurrent $j_{ph}$ minus the recombination current, and the current of the excess electrons extracted from the contact. Hence

$$j = j_{ph} - j_{rec0} e^{q(V + V_s)/kT} + C_i \frac{dV_s}{dt}$$

(8)

**Impedance Model.** For calculating the IS response of the previously presented SPM, a small ac perturbation (denoted by tilde) of angular frequency $\omega$ is applied to the voltage, added to the steady-state characteristic (indicated by overbar). By taking the Laplace transform, the small amplitude current is

$$\hat{j} = \hat{j}_{rec} \left( \frac{qV}{\gamma kT} + \frac{qV}{\beta kT} \right) + i\omega C_i \hat{V}_s$$

(9)

The small perturbation surface polarization voltage is calculated by taking a Laplace transform of the eq 4

$$\hat{V}_s = \frac{\hat{V}}{1 + i\omega \tau_{kin}}$$

(10)

By substituting eq 10 in eq 9, the following expression for the ac impedance is obtained

$$Z = \frac{\hat{V}}{j} = \left[ i\omega C_i + \frac{1}{R_L + i\omega L} + \frac{1}{R_{rec}} + \frac{1}{R_C - i\omega \tau_{kin}} \right]^{-1}$$

(11)

where the equivalent circuit elements have the following values in terms of model parameters

$$R_{rec} = \frac{\beta kT}{q\tau_{rec}}$$

$$R_{C} = \frac{\gamma kT}{q\tau_{rec}}$$

$$L = \tau_{kin} R_L$$

$$R_C = \frac{b\tau_{kin}}{C_i}$$

(12)

A representation of the model of eq 11 as an equivalent circuit is shown in Figure 2. In this circuit, $R_s$ is a series resistance and $R_{rec}$ is a recombination resistance that is inversely related to the steady-state recombination current density $j_{rec0}$. The capacitance $C_d$ is added to represent the dielectric bulk (or surface) processes that usually occur at high frequency. $R_L$ is

Figure 1. Energy diagram of a perovskite solar cell in which electron-selective contact locates at the left and hole-selective contact locates at the right side. (a) Equilibrium condition in the dark. (b) Open circuit under illumination condition. $E_g$, $E_V$: Edges of conduction and valence bands. $E_g$: Fermi Level. $E_s$, $E_i$: Quasi-Fermi level of electrons and holes. $V$: External voltage of the contacts. $V_s$: The constant built-in voltage. $V_t$: The variable surface polarization voltage. Indicated in panel b are the accumulation of holes and cations and the tunnelling of electrons across the surface barrier.

$$Q_s = qP_s = Q_{so} e^{qV_s/kT}$$

(1)

as a function of surface hole density, $P_s$, the elementary electrical charge, $q$, thermal energy $kT$, and the equilibrium surface charge $Q_{so}$. The capacitance associated with surface charging is

$$C_i = \frac{dQ_s}{dV_s} = \frac{qQ_{so} e^{qV_s/kT}}{\gamma kT}$$

(2)

The exponent $\gamma$ takes the value of 2 in the case of purely electronic accumulation capacitance. Under equilibrium condition at a given voltage $V$

$$V_s = V - V_{bi}$$

(3)

where $V_{bi}$ is a built-in voltage. The presence of ions at the interface implies that the build up and recovery of the equilibrium distribution is severely impeded by the rate of ion migration. Thus the internal voltage $V_s$ cannot follow the external voltage instantaneously but reacts slowly to achieve the condition imposed by $V$. This characteristic behavior has been described by a relaxation equation of the type

$$\frac{dV_s}{dt} = - \frac{V_s - (V - V_{bi})}{\tau_{kin}}$$

(4)

where the relaxation kinetic constant $\tau_{kin}$ is determined by the rapidity of ion displacement at the specified illumination and temperature.

Next, we establish the standard photovoltaic properties of the solar cell to form a diode equation. Recombination current at the surface of the cell depends on electron and hole concentration

$$I_{rec} = k_{rec} n Q_s$$

(5)

with a recombination rate constant $k_{rec}$. The bulk electron density is $n = n_0 \exp(qV/\beta kT)$, and hence the recombination current under transient condition is

$$I_{rec} = j_{rec0} e^{qV_s/\beta kT} e^{q(V + V_s)/\beta kT}$$

(6)

Figure 2. Equivalent circuit obtained by applying a small ac perturbation. In this circuit, $R_s$ is the series resistance, $C_d$ is the dielectric capacitance, $R_{rec}$ is the recombination resistance, $R_s$ is the series resistance with the inductance $L$, and $R_C$ is the series resistance with the surface charging capacitance $C_i$. 

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Therefore, the value of the series resistance with the inductance $L$, and both of them are inversely proportional to $J_{\text{rec}}$. The inductance $L$ has a direct dependence on the $\tau_{\text{kin}}$. $R_C$ is the series resistance with the capacitance $C_1$, and it is also directly dependent on the $\tau_{\text{kin}}$, and an additional parameter $b$ that is justified below.

The physical interpretation of the circuit is the following. The parallel $R_{\text{rec}} - C_3$ combination is the standard ac circuit for a solar cell governed by recombination. For a perovskite solar cell the recombination may fluctuate from bulk to surface-dominated process depending on specific conditions. In parallel to the usual solar cell elements, there are two more circuit branches that correspond to the accumulation and extraction of charge from the surface. First, the branch $R_{\text{rec}} - C_1$ is the charging and discharging of the surface accumulation capacitance controlled by the kinetic relaxation time $\tau_{\text{kin}}$. The second branch $R_L - L$ is an additional nonstandard process. This is a remarkable feature of the model that follows directly from eq 4. As we explained before, there is a delay for the surface charging with respect to external voltage because of the ions movement that governs the equilibration of the interface controlled by the kinetic relaxation constant $\tau_{\text{kin}}$. This delay time is the reason for the inductive line in the equivalent circuit.

**Interpretation of Impedance Spectra.** In Figure 3 we show the characteristic spectra associated with the impedance model. We also indicate the values of low- and high-frequency resistances. At the low-frequency region, the inductance and the capacitances act as a short circuit and open circuit, respectively. Therefore, the value of the $Z'$ at the end point of the spectra is given by the series-parallel combination $R_{\text{rec}} = R_i + R_1 || R_{\text{rec}}$. At the high-frequency region, $R_{\text{rec}} = R_1$.

The first spectrum (a) shows two positive arcs. The combination of resistances $R_{\text{rec}}$ and $R_i$ determines the diameter of the arcs. This type of spectra has been found in many works of IS of the perovskite solar cells, and it is often observed that the two arcs have similar width and vary in a coupled way when the voltage or illumination is changed. We note that in the model $R_{\text{rec}}$ and $R_i$ show a similar voltage dependence, which may explain the unisonous variation of the distinct low-frequency arcs frequently observed in the literature.

By increasing the value of $\tau_{\text{kin}}$, and the capacitance $C_1$, a positive inductive loop appears in the impedance spectrum (b). The inductance becomes more dominant for larger values of the kinetic relaxation constant. Then, the loop becomes bigger and crosses the axis, entering negative capacitance values (c). When the kinetic relaxation constant is increased to large values (here 100 s), the low-frequency arc goes into negative capacitance values (d), a behavior that is well documented. These two significant impedance spectra, that is, the inductive loop and the negative capacitance at low frequency, are explained theoretically for the first time.

**Figure 4** shows the capacitance–frequency ($C$–$f$) plots for the complex impedance spectra of Figure 3, where the real part of the capacitance is taken from the complex capacitance $C = C'$.

**Figure 3.** Typical complex plane impedance plots obtained for different values of kinetic relaxation constant $\tau_{\text{kin}}$ at different applied biases for the following values of $V_{\text{in}} = 0.5 \, \text{V}$, $V_{\text{oc}} = 0.95 \, \text{V}$, $\phi = 30$, $f_{\text{ph}} = 20 \, \text{mA cm}^{-2}$, $\gamma = 2$, $\beta = 1$, $k_B T/q = 0.026 \, \text{eV}$, area = 0.1 cm$^2$ and the following values for the resistances and capacitances $R_{\text{rec}} = R_i = 100 \, \Omega$ cm$^2$, $R_L = R_{\text{rec}} || R_i = 96.3 \, \Omega$ cm$^2$, $C_{\text{bulk}} = 10^{-7} \, \text{F cm}^{-2}$ and the other values for (a) $\tau_{\text{kin}} = 0.1 \, \text{s}$, $L = 25.88 \, \text{H cm}^{-2}$, $R_C = 200 \, \Omega$ cm$^2$, $C_1 = 5 \times 10^{-4} \, \text{F cm}^{-2}$, (b) $\tau_{\text{kin}} = 1 \, \text{s}$, $L = 258.8 \, \text{H cm}^{-2}$, $R_C = 10 \, \Omega$ cm$^2$, $C_1 = 0.1 \, \text{F cm}^{-2}$ (inset shows the zoomed-in view of the positive loop), (c) $\tau_{\text{kin}} = 10 \, \text{s}$, $L = 2588 \, \text{H cm}^{-2}$, $R_C = 100 \, \Omega$ cm$^2$, $C_1 = 0.1 \, \text{F cm}^{-2}$, and (d) $\tau_{\text{kin}} = 100 \, \text{s}$, $L = 25880 \, \text{H cm}^{-2}$, $R_C = 10 \, \text{kΩ cm}^{-2}$, $C_1 = 0.01 \, \text{F cm}^{-2}$.

**Figure 4.** Capacitance–frequency ($C$–$f$) spectra are calculated for the spectra of Figure 3. The “blue”, “red”, “green”, and “black” curves show the $C$–$f$ plot of the Figure 3a–d, respectively.
1/ωZ. The low-frequency part of the curves corresponds to the capacitance $C_1$, and the high-frequency part shows the dielectric capacitance. In the cases with negative capacitance the undershoots in the curves correspond to the transition to negative capacitance in Figure 3. Also, an undershoot appears in plot (b) at frequencies that the positive loop gets very close to the frequency axis.

To establish the suitability of the model for the description of experimental results, we have analyzed previously reported impedance spectra. The spectra have been measured in perovskite solar cells with special electron-selective contact consisting of a periodic multilayered structure that magnifies the effects of the interface. The sequential deposition of SiO$_2$ and TiO$_2$ mesoporous layers forces multiple electron injection processes that cause very large loop features in the impedance plots.

In Figure 5 we show two characteristic spectra, and the fitting with the equivalent circuit of the SPM provides the results indicated in Table 1. Values of $\tilde{f}_{rec}$ and $C_1$ are of the same order of magnitude in both cases. Values of $\tau_{kin}$ are similar to those previously obtained in the fitting of the dynamic hysteresis of the $j$–$V$ curves in our previous work. We take the agreement of very different experimental methods as encouraging support about the behavior of the interfaces of perovskite solar cells.

Table 1. Values Calculated from the Fittings of the IS Data of Two Perovskite Solar Cells to the Equivalent Circuit of Figure 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tilde{f}_{rec}$ (mA/cm$^2$)</th>
<th>$C_4$ (F cm$^{-3}$)</th>
<th>$C_1$ (F cm$^{-3}$)</th>
<th>$\tau_{kin}$ (s)</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1$</td>
<td>0.012</td>
<td>1.11 x 10$^{-5}$</td>
<td>1.38 x 10$^{-5}$</td>
<td>28.2</td>
<td>0.12</td>
</tr>
<tr>
<td>$S_2$</td>
<td>0.027</td>
<td>2.54 x 10$^{-5}$</td>
<td>0.011</td>
<td>23</td>
<td>0.19</td>
</tr>
</tbody>
</table>

of magnitude in both cases. Values of $\tau_{kin}$ are similar to those previously obtained in the fitting of the dynamic hysteresis of the $j$–$V$ curves in our previous work. We take the agreement of very different experimental methods as encouraging support of the SPM based on eq 4. The SPM generates the equivalent circuit of Figure 2 with the parameter $b$ in eq 12 having a value 1. However, we note in Table 1 that the experimental value of the parameter $b$ is around 0.1 to 0.2 in both cases. The interpretation of this finding is the following. The equivalent circuit is generated from the theory with a restricted number of parameters of the model, which are essentially three, namely, the recombination current density $\tilde{J}_{rec}$ the kinetic relaxation constant $\tau_{kin}$ and $C_{id} = qQ_0/k_BT$. It appears that the equivalent circuit describes well the experimental data, but the additional parameter $b$ is needed to generate a richer set of spectra. This is far from surprising, as the previously formulated SPM incorporates a kinetic delay of charge at the surface but not the energy loss process across the interface such as electron transfer by tunneling suggested in Figure 1. The departure of $b$ from the value 1 indicates that the spectra possess additional physical characteristics that need to be described by a more general model. We suggest that a resistive process for charge transfer across the interface may be needed, in agreement with the usual observation of a major decrease in photocurrent in the presence of poorer contacts, which causes a substantial decrease in solar cell performance. To such an end systematic experimental analysis is required that is beyond the scope of this work.

In summary, we have developed new implications from a SPM that assumes a kinetic delay of the state of the interface by slow buildup of ionic charge. Previously the model was used to describe dynamic hysteresis in the voltage sweep curves, and here we found the characteristics of IS, which bring about two conclusions. First, because of the peculiar kinetic delay, the surface processes produce a highly structured spectral shape consisting of at least two impedance arcs, which will vary in coordination, because they reflect unique underlying characteristics. The second conclusion is the appearance of inductive loops, either positive or negative capacitance, that have been widely observed previously in the experimental reports. We show that the loops contain important kinetic information about the behavior of the interfaces of perovskite solar cells. The fitting of data suggests that the experimental response is even richer than that covered by our model, indicating the need

Figure 5. Impedance and capacitance–frequency ($C$–$f$) spectra obtained under illumination and with an applied bias of 0.7 V. (a,c) Complex impedance plots of two different perovskite samples $S_1$ (green) and $S_2$ (red). (b,d) Their ($C$–$f$) plots, respectively. The circles represent the experimental points, while solid lines are the fitting curves using the equivalent circuit. (a) $R_L = 33.8$ Ω cm$^2$, $R_{rec} = 4700$ Ω cm$^2$, $C_3 = 1.11 \times 10^{-5}$ F cm$^{-2}$, $R_L = 4350$ Ω cm$^2$, $L = 123$ kH cm$^{-1}$, $R_L = 2460$ Ω cm$^2$, $C_1 = 1.38 \times 10^{-5}$ F cm$^{-2}$, (c) $R_L = 19.6$ Ω cm$^2$, $R_{rec} = 219$ Ω cm$^2$, $C_4 = 2.54 \times 10^{-5}$ F cm$^{-2}$, $R_L = 2$ kΩ cm$^2$, $L = 45$ kH cm$^{-1}$, $R_L = 390$ Ω cm$^2$, $C_1 = 0.011$ F cm$^{-2}$. DOI: 10.1021/acs.jpclett.7b00415
for extensive studies to clarify the complex behavior of the perovskite solar cell.

**AUTHOR INFORMATION**

**Corresponding Author**
E-mail: bisquert@uij.es.

**ORCID**
Agustín Bou: 0000-0002-7535-5063
Saeed Olyaee: 0000-0002-6154-7646
Juan Bisquert: 0000-0003-4987-4887

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