

I – V relations in semiconductors with ionic motion*

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Abstract Semiconductors with mobile donors and acceptors are mixed-ionic-electronic-conductors, MIECs, which exhibit peculiar electronic (electron/hole), I_e , current-voltage relations. This is a result of the redistribution of the ions under the applied electrical potential. MIECs are usually ionic materials which exhibit relative low electron/hole mobilities as compared to the materials used in the semiconductor industry. However, thin layers of MIECs exhibit a low resistance and fast response and become of increasing interest.

The I_e – V relations are discussed for a few typical examples. It is shown that they depend on the energy band gap as when it is large, the semiconductor is either p-type or n-type. The I_e – V relations depend also on the nature of the electrodes, whether blocking for ion exchange or not. Experimental results for Cu_2O are presented and analyzed using one of the models discussed.

Keywords I-V relations · MIEC · Semiconductor · PLEC · Cu_2O

1 Introduction

I – V relations in semiconductors with mobile donors and/or acceptors are quite different from those with frozen ionic defects. Under an applied voltage the ionic defects redistribute in the bulk. This may occur when the electrodes exchange freely ions with the bulk and it must occur when they block ion exchange. I_e , the electronic (electron/hole) part of the

current, is affected by the redistribution of the ionic defects. The I_e – V relations are, in many cases, non linear. We emphasize that the non linearity originates from the redistribution of the ions in the bulk and is not due to a space charge at the boundaries. The materials that conduct both electrons/holes and ions are known as mixed-ionic-electronic-conductors, MIECs.

Most MIECs are ionic solids which exhibit electron/hole small polaron, hopping, conduction and thus have relatively low mobility and conductivity as compared to materials used in the semiconductor industry. However, thin films of these materials, that can now be prepared routinely, exhibit a low resistance and allow for high current densities and fast response in electronic circuits. It is this and the fact that their defect distribution and I_e – V relations can be tuned, that their electronic properties become of interest.

In addition to the effect on bulk properties, MIECs may exhibit different contact properties. In the presence of a high concentration of ionic defects any space charge region at the boundaries is thin and may allow for electron tunneling. In this case the electrodes are ohmic with respect to electron exchange.

In other cases, with lower concentrations of the mobile charge carriers, one has to examine the effect of the motion of the ions on the work function and the Debye length and thus on the interface properties. The discussion has also to consider the boundary conditions whether the electrodes are inert or chemically active, as well as the nature and relative concentrations of the defects whether due to doping or deviation from stoichiometry or whether due to ion pair production.

Last, one has to examine the diffusion length for recombination of electrons/holes and compare it with the scattering length and the Debye length. In ionic crystals electron hole propagate with relatively low mobility. There may be states

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in the forbidden energy band gap that allow fast recombination. Under proper conditions an extended diffusion length for recombination which is longer than the Debye length, as in the classical pn and Schottky junctions, need not be found.

We here concentrate on the effect of the mobility of the ionic defects on the bulk properties of the MIEC and the corresponding electronic current vs. voltage, I_e-V , relations. Local neutrality is assumed. Space charge effects are neglected. The effect of the redistribution of the mobile ionic defects on the bulk I_e-V relations depends on the nature of the system and does not follow a general rule. The key differences are two: (a) Can both holes and electrons be generated at the two opposite sides of the sample under oxidizing and reducing conditions or does one of the electronic charge carriers stay dominant due to a large energy band gap. This is of special interest when the donors and acceptors are native ones. (b) Are the electrodes blocking for ions. If both native defects (acceptors and donors) exist then not only the distribution of defects but also their total number depends on the applied voltage. Two possible realizations are mentioned. One is the polymer light emitting electrochemical cell, PLEC, which corresponds to the first case (both acceptors and donors are generated). The $I-V$ relations diverge exponentially under high applied voltage, when using ion blocking electrodes. The other is Cu_2O which seems to correspond to the second case with holes only. The corresponding $I-V$ relations exhibit saturation (current limitation) under high applied voltage and ion blocking electrodes.

The question of whether both acceptors and donors may appear or only one type and the reversibility of the electrodes are not the only considerations. The ratio of the concentration of the different charge carriers, as well as the existence of other immobile charged defects affect the I_e-V relations as well.

2 Assumptions of the discussion

The following assumptions are made in the discussion below:

- I) The electrodes are reversible with respect to electron exchange.

An electrode is defined as reversible when local equilibrium prevails at all sites near the interface, also under current. For electron exchange it is well known that this may not be the case and recombination may occur only after an electron has diffused to a distance as far as $\sim 1 \mu\text{m}$ from the interface. (For ion exchange deviation from local equilibrium will occur on a much shorter distance which can be as low as an atomic layer, $\sim 0.17 \text{ nm}$, near the interface.) In reality one does not require strict local equilibrium and may allow a small departure

from it. This is the case when the impedance of the bulk is dominant, limiting the current to values for which the electrode I_e-V relations are linear.

- II) Local equilibrium prevails in the bulk.
- III) Local neutrality.

Local or, at least, quasi local neutrality is assumed. Quasi local neutrality occurs when the difference between the positive and negative charge densities is much smaller than each of them [1]. Quasi neutrality is violated only when the gradients in the charge density are high and the characteristic length of the gradients is shorter than a screening length [1]. This occurs at abrupt interfaces. It may also occur within the bulk when the applied electric field or chemical potential difference is excessively high to induce a large gradient in the charge density there. As we discuss the bulk properties and limit the applied potential differences, quasi local neutrality may be assumed.

- IV) The electrodes are either reversible or, on the contrary, strictly blocking for ion exchange. The relevant condition will be indicated.

3 Semi-conductors with mobile donors or acceptors

3.1 Motion under an applied voltage

Figure 1(a) presents, schematically, a semi-conductor with donors and electrons excited into the conduction band. Under an applied voltage, with the polarity as indicated, the electrons will move to the right. The donors, which are assumed to be mobile, will move either to the right or to the left. The ionic defects are driven not only by the applied voltage but also by the chemical potential difference of the chemical component that contributes the donors. Thus if the electrodes are not inert the chemical potential difference that they impose on the bulk has to be taken into consideration as well. This can easily be seen by examining the current density equations [2]. This yields, in the steady state, for the

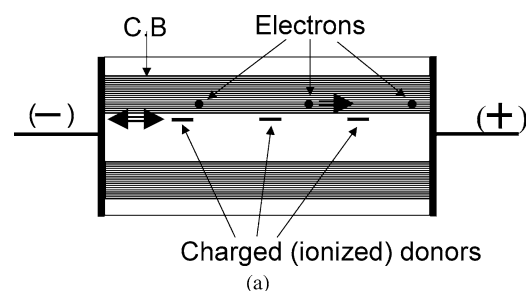


Fig. 1a Mobile donors and electrons in an n-type semiconductor under an applied voltage. C.B.- conduction band

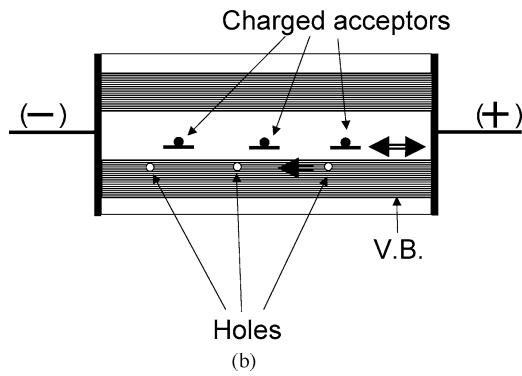


Fig. 1b Mobile acceptors and holes in a *p*-type semiconductor under an applied voltage. V.B. – valence band

electron current within the MIEC:

$$I_e = -\frac{V}{R_e} \tag{1}$$

and for the mobile donor current:

$$I_d = \frac{V_{th} - V}{R_d} \tag{2}$$

where R_e and R_d are positive parameters which represent the resistance of the bulk to electron and donor current, respectively, V is the voltage drop across the bulk and V_{th} is fixed by the difference, across the bulk, in the chemical potential, μ_D , of the neutral component that provides the charged donors:

$$V_{th} = -\frac{\Delta\mu_D}{zq} \tag{3}$$

where q is the elementary charge and z is the valence state of the mobile ion. Thus it is evident that the driving force for the ions is a combination of the voltage V and the chemical potential difference $\Delta\mu_D$. The difference $V_{th} - V$ may have a different polarity than V . Similar arguments hold for acceptors and holes, Fig. 1(b).

3.2 Nature of the donors and acceptors

The donors and acceptors can be either impurities introduced into the semiconductor by doping or be native ionic defects. An example for the first kind is Li in Si. The Li impurity is ionized to yield a free electron in the Si conduction band: $\text{Li} \rightarrow \text{Li}_i^+ + e^-$ (We use here the Kröger-Vink notation of defects) [3]. The Li_i^+ ion is somewhat mobile even at room temperature and quite mobile above 70°C [4]. It should be noticed that doping does not always result in the generation of comparable amounts of (quasi free) electrons or holes in the conduction or valence band, respectively. The reason is that the dopant may be self compensated by ionic defects rather than electronic ones [5].

In compounds native defects, originating from deviation from stoichiometry, also contribute quasi free electrons or holes. The ionic defects are then considered as native donors or acceptors. For example, oxygen vacancies, $V_O^{\bullet\bullet}$, in $\text{CeO}_{2-\delta}$, and interstitial silver ions, Ag_i^\bullet , in $\text{Ag}_{2+\delta}\text{S}$ are donors, while silver vacancies, V_{Ag}^\backslash in $\text{Ag}_{2+\delta}\text{S}$, copper vacancies, V_{Cu}^\backslash , in Cu_2O as well as oxygen interstitials, $O_i^{\backslash\backslash}$, in Cu_2O , are acceptors.

4 $I_e - V$ relations

4.1 General

The $I_e - V$ relations are linked to the distribution of ionic defects which act as donors or acceptors. As local neutrality is assumed the concentration of the electrons or holes follow this distribution. The distribution need not always depend on the applied voltage. This may, sometimes, be the case when both electrodes are reversible with respect to ion exchange (in addition to being reversible with respect to electron exchange, which is always assumed in this paper). However, the defect distribution depends on V in all cases when one or both electrodes are blocking for ion exchange. We shall demonstrate this by referring to well known, specific, defect models.

4.2 Defect models to be considered

- I) $p \ll n \ll N_{\text{ion}}$, (or $n \ll p \ll N_{\text{ion}}$) where p , n and N_{ion} are the hole, electron and ion concentration, respectively. As an example serves $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$. This material conducts (at elevated T) oxygen vacancies and under reducing conditions exhibits also a significant electron conductivity which may exceed the ionic one. Under high, ~ 1 atm, oxygen partial pressure the electronic conductivity is negligible.
- II) $p, n \ll N_{\text{ion}}$, e.g. $\text{Y}_{0.2}\text{Zr}_{0.8}\text{O}_{2-\delta}$ (YSZ), which (at elevated T) conducts oxygen vacancies, $V_O^{\bullet\bullet}$, and under reducing conditions exhibits also a small electron conductivity while under oxidizing conditions it exhibits also a small hole conductivity. Another example is a quasi MIEC, a blend of two polymers one conducting ions and the other conducting electrons and holes [6]. A specific example is the electron conductor, conjugated polymer PPV and the electrolyte polymer PEO, doped with a Li salt in the ratio: PPV:PEO:Li 55:5:1 [7]
- III) $p \ll n \sim N_{\text{ion}}$, e.g. $\text{CeO}_{2-\delta}$. This material conducts (at elevated T) both oxygen ions and electrons under reducing conditions.

An equivalent model is $n \ll p \sim N_{\text{ion}}$, e.g. Cu_2O and $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$. Cu_2O conducts copper vacancies, V_{Cu}^\backslash , and holes [8, 9] and YBCO conducts holes and oxygen

interstitials, O_i^{\ll} [10]. Ionic motion is observed both at elevated T as well as at room temperature.

4.3 The significance of the nature of the electrodes with respect to ion exchange

We identify three situations with respect to ion exchange at the electrodes (while they are reversible with respect to electron exchange):

- I) Two reversible electrodes with respect to ion transfer.
- II) One reversible electrode and one ion blocking.
- III) Two ion blocking electrodes.

Under the reversible electrode the stoichiometry (and thus the defect concentration) in the bulk at the boundary, is fixed by the interaction with the surrounding/electrode and does not change under current. The distribution of defects within the bulk MIEC may change with the applied voltage even when two reversible electrodes are used. These electrodes pin only the boundary values of the defect distribution.

Example 1. The defect distribution for the defect model $p \ll n \ll N_{ion}$ e.g. of the Galvanic cell:

$$P(O_2)^{low}, Pt|Gd_{0.2}Ce_{0.8}O_{2-\delta}|Pt, P(O_2)^{high},$$

$$V_{th} = \frac{k_B T}{4q} \ln \frac{P(O_2)^{high}}{P(O_2)^{low}} \tag{4}$$

where T is the temperature and k_B the Boltzmann constant. With the local neutrality condition $[Gd_{Ce}^{\ll}] + n = [V_O^{\bullet\bullet}]$, the electron distribution can be expressed analytically [2]. It is shown in Fig. 2. While the boundary values, n_0, n_L , are pinned by the reversible electrodes, the distribution of electrons within the MIEC depends on the applied voltage.

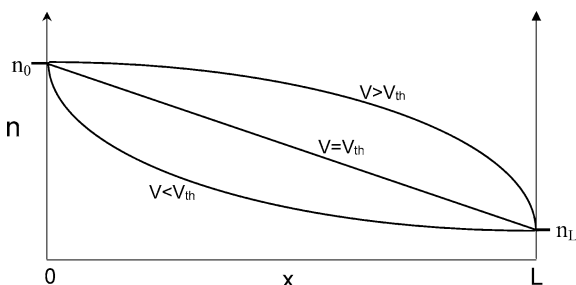


Fig. 2 Electron distribution (qualitative) for the defect model $p \ll n \ll N_{ion}$ forming a graded n-type MIEC. The MIEC is at $0 < x < L$. The voltage is applied on electrodes at $x = 0$ and L .

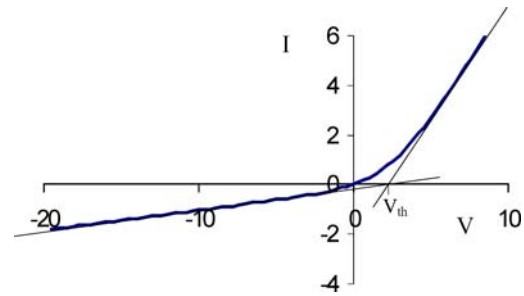


Fig. 3 $I_e - V$ relations of Eq. (5), for a cell based on a MIEC with the defect model $p \ll n \ll N_{ion}$, using two reversible electrodes with respect to both electron and ion exchange. Voltage and current: arbitrary units.

Since the electron distribution changes with V , hence the $I_e - V$ relations are not linear: [2]

$$I_e = -S\sigma_e^0 \frac{V_{th} - V}{L} \frac{e^{-\beta q(V_{th} - V)} - e^{-\beta q V_{th}}}{1 - e^{-\beta q(V_{th} - V)}},$$

$$\sigma_e^0 = q\nu_e n_0 \tag{5}$$

where S is the cross sectional area of the MIEC, σ_e^0 is the electron conductivity at $x = 0$, ν denotes mobility and $z = 1$. The $I_e - V$ relations are shown in Fig. 3. It is noticed that the asymptotic $I_e - V$ relations are linear with different slopes for $V > 0$ and $V < 0$ due to different non-stoichiometry (see also Fig. 2).

When the same material is placed between one reversible electrode and one ion blocking, the $I_e - V$ relations become exponential. They can be derived from Eq. (5) under the condition $V = V_{th}$, which is the condition for zero ionic current, (Eq. (2)) [11]. For an n-type MIEC this yields,

$$I_e = -S \frac{k_B T}{qL} \sigma_e^0 (1 - e^{-\beta q V}), \quad V_{min} < V < V_{max},$$

$$p \ll n \ll N_{ion} \tag{6}$$

This looks like the I-V relations for a Schottky barrier or pn junction but they are not. They originate from the bulk properties of the MIEC. Furthermore, the applied voltage is limited by decomposition/electroplating. The later limitation is a result of the changes in the chemical potential of the mobile component associated with the redistribution of the mobile defects and local neutrality.

When the same MIEC (of the defect model $p \ll n \ll N_{ion}$) is placed between two ion blocking electrodes, then the $I_e - V$ relations change dramatically to become current limited instead of exponential:

$$I_e = -S2 \frac{k_B T}{qL} \bar{\sigma}_e \tanh \left\{ \frac{qV}{2k_B T} \right\},$$

$$|V| < \min \{ |V_{min}|, |V_{max}| \}, \quad \bar{\sigma}_e = q\nu_e \bar{n} \tag{7}$$

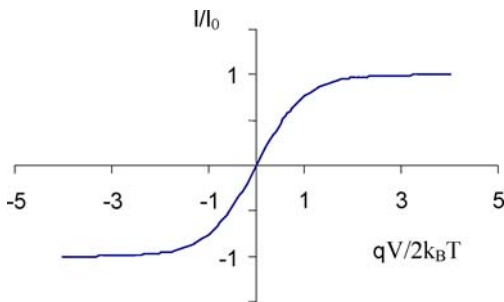


Fig. 4 The I_e – V relations of Eq. (7), for a cell based on a MIEC with the defect model $p \ll n \ll N_{ion}$, using two ion blocking electrodes

where \bar{n} is the average value of n (equal to the uniform value under zero voltage). The I_e – V relations of Eq. (7) are exhibited in Fig. 4.

Example II. In the former examples the defect distribution depends on the applied voltage whether the electrodes are reversible or not (though in a different way). As a result the I_e – V relations are non linear for all three electrode conditions, I–III. In the next example the defect distribution is independent of the voltage when both electrodes are reversible for ion exchange. Under this condition the I_e – V relations are linear. However, when at least one electrode is ion blocking, then the defect distribution depends on the voltage and the I_e – V relations are not linear. Again there is a significant difference between the case with one ion blocking electrode and two blocking electrodes.

The defect model now is $p \ll n \sim N_{ion}$, or $n \ll p \sim N_{ion}$. For example, $Cu_{2-\delta}O$ was shown, at elevated temperatures, to be a p-type semiconductor with V_{Cu} as mobile acceptors [8] and to conform to the defect model $n \ll p \sim N_{ion}$. We assume that this holds also down to room temperature. Above $\sim 800^\circ C$ oxygen interstitials contribute also to the acceptor concentration and the defect model is more complex [8]. The cell that serves as an example is:

$$P(O_2)^{low}, E_1 | Cu_{2-\delta}O | E_2, P(O_2)^{high} \quad (8)$$

The hole distribution is independent of the voltage for reversible electrodes, as exhibited in Fig. 5, with the boundary values p_0, p_L fixed by the reversible electrodes [2].

The distribution becomes dependent on the voltage when at least one electrode blocks ions. Figure 6 shows the distribution when one electrode (at $x = L$) blocks ions. For each V value the distribution is linear. However the slope changes with V . The value of p under the reversible electrode (at $x = 0$) is pinned. Figure 7 shows the distribution when both electrodes block ions. For each V value the distribution is linear. However, the slope changes with V . The overall amount of the holes is fixed by the history of the sample.

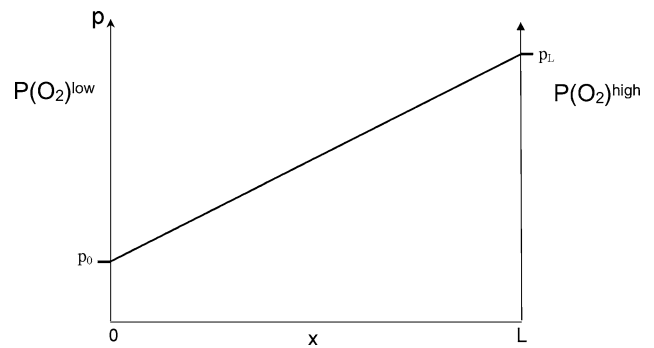


Fig. 5 Hole distribution in a MIEC conforming to the defect model $n \ll p \sim N_{ion}$ with reversible electrodes, E.g. the cell of Eq. (8). The distribution is independent of the applied voltage

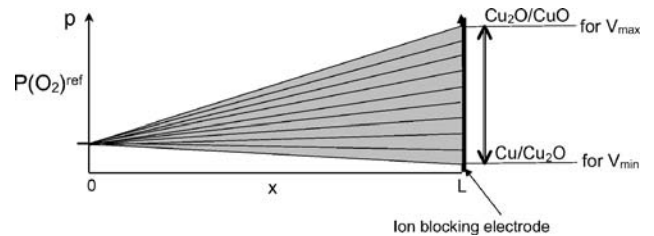


Fig. 6 Hole distribution in a MIEC of the $n \ll p \sim N_{ion}$ defect model, e.g. $Cu_{2-\delta}O$, under an applied voltage when one electrode (at $x = L$) is blocking ions. The lines represent the distribution for different V values. The range of the allowed applied voltage is limited to avoid the formation of a new phase under the blocking electrode, Cu for low V and CuO for high V .

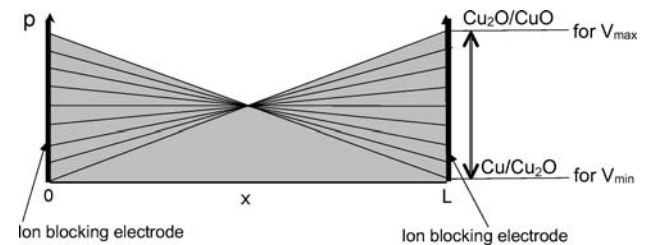


Fig. 7 Hole distribution in a MIEC of the $n \ll p \sim N_{ion}$ defect model, e.g. $Cu_{2-\delta}O$, under an applied voltage when both electrodes block ions. The lines represent the distribution for different V values. The range of the allowed applied voltage is limited to avoid the formation of a new phase under the blocking electrode, Cu for low V and CuO for high V .

The I_e – V relations for the last two cases are not linear as the distribution depends on V . The I_e – V relations when one electrode is ion blocking, are exponential [2, 12]:

$$I_e = -S2 \frac{k_B T}{qL} \sigma_e^0 (1 - e^{-\beta qV/2}) \quad (9)$$

as can be derived from the expressions developed in [2] substituting $V_{th} = V$ for zero ionic current, while keeping the composition at one electrode (at $x = 0$) fixed.

The $I_e - V$ relations are very different when both electrodes block ions [2, 12]:

$$I_e = -S4 \frac{k_B T}{qL} \bar{\sigma}_e \tanh \left\{ \frac{qV}{4k_B T} \right\},$$

$$|V| < \min \{ |V_{\min}|, |V_{\max}| \}, p \ll n \sim N_{\text{ion}} \quad (10)$$

These relations exhibits current limitation. The limitation is due to the decrease in the hole concentration, p , on one side without significant generation of electrons (due to a large energy gap). This increases the resistance on that side to an extent that the current becomes limited. Eq. (7) is different from Eq. (10) in a few coefficients only.

5 The defect distribution in a MIEC with holes, electrons and mobile ions, of the type $p, n \ll N_{\text{ion}}$

The defect distribution is shown in Fig. 8. There is an n region near one reversible electrode and a p region near the opposite one. The boundary values are pinned by the reversible electrodes. However, the distribution depends on the applied voltage. Therefore the $I_e - V$ relations are not linear. Qualitatively they look as the ones in Fig. 3 [13]. The distribution for zero ionic current corresponds to the one given by the single value $V = V_{th}$. However, with ion blocking electrodes the boundary values under the blocking electrodes depend on the applied voltage and are not fixed. For one ion blocking electrodes the Hebb-Wagner relations are obtained [14, 15]:

$$I_{el} = -S \frac{k_B T}{L} [v_n p_0 (e^{\beta q V} - 1) - v_e n_0 (e^{-\beta q V} - 1)] \quad (11)$$

where, $z = 1, j_{el}$ is the total electronic current contributed by both electrons and holes, and the reversible electrode is the one at $x = 0$. For two ion blocking electrodes the I-V

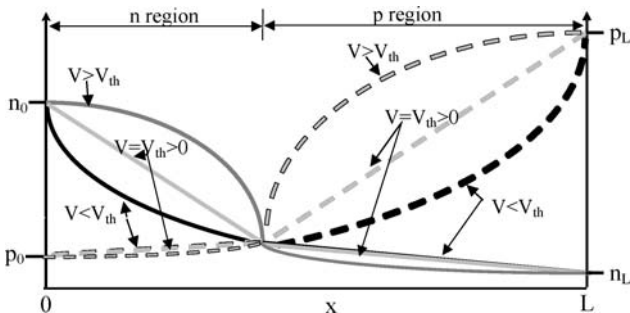


Fig. 8 . Electron, n , and hole, p , distribution (qualitative) in a MIEC of the defect model $p, n \ll N_{\text{ion}}$. Solid line: n , dashed line: p . The distribution changes with the applied voltage V . The ionic defects follow by local neutrality.

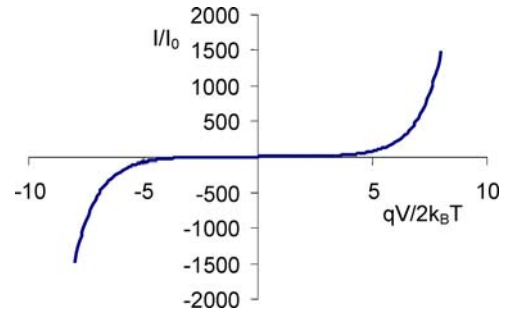


Fig. 9 . $I_e - V$ relations for a MIEC of the $n, p \ll N_{\text{ion}}$ defect model with two ion blocking electrodes, Eq. (12).

relations are approximately [16],

$$I_{el} = I_0 \text{Sinh}(\beta q V / 2) \quad (12)$$

where I_0 is independent of V . These relations are exhibited in Fig. 9. The current diverges exponentially with V for both voltage polarities in contrast to the limited current obtained in the two cases discussed before. The difference can be traced back to the fact that now a decrease of say donors on one side and the lowering of the electron concentration there results in a significant increase in the hole concentration according to the mass action law:

$$pn = n_i^2 \quad (13)$$

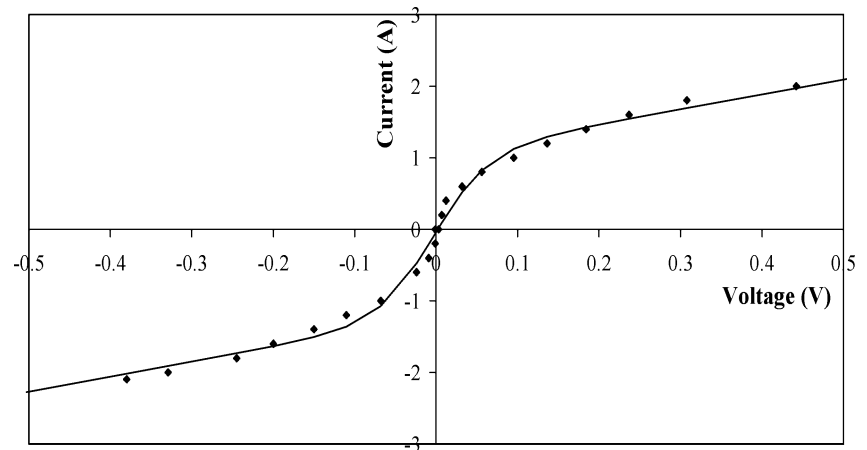
where $n_i \propto \exp\{-E_{\text{gap}}/2k_B T\}$ is the intrinsic electron and hole concentration. Assuming a lower energy gap, E_{gap} , between the conduction and valence bands for the present MIEC as compared to the former MIECs discussed, then p cannot be neglected when n becomes small and vice versa.

This defect model, $p, n \leq N_{\text{ion}}$, has been realized by a quasi MIEC composed of two phase intimately mixed [7]. One phase is a polymer that conducts electron/holes and the other a polymer that conducts ions. The $I_e - V$ relations exhibited by a cell based on this mixture were analyzed in terms of Eq. (12) [16].

6 Experimental $I_e - V$ relations for Cu_2O placed between two ion blocking electrodes

So far the discussion was theoretical. We now present experimental results of $I_e - V$ measurements on the MIEC Cu_2O placed between two ion blocking electrodes, done at room temperatures. The experimental and theoretical details are given elsewhere [9, 17, 18]. The $I_e - V$ results are exhibited in Fig. 10. It turns out that the $I_e - V$ relations depend on the rate of voltage scan. This supports the claim that polarization is taking place in which ions are slowly redistributing

Fig. 10 . I_e – V relations of the cell Cu|Cu₂O|Ag, at room temperature. Both electrodes are considered as ion blocking at this temperature.



within the bulk, under the applied electrical potential. Indeed a slow measurement, with a full voltage scan taking 33 h (presented in Fig. 10) complies with the limiting current relations, Eq. (10) that hold for the relevant defect model. A fast measurement (3 h) on the same cell, yields almost linear relations (not shown) indicating that the ions do not have time to redistribute during the voltage scan. There is one difference between the results and Eq. (10) namely that the \tanh relations are skewed. This was explained to be due to the presence of additional immobile acceptors that contribute additional holes and a parallel ohmic current (linear $I_e - V$), [18].

7 Summary

The electronic (electron/hole) current vs. voltage in mixed-ionic-electronic-conductors was discussed by analyzing typical examples of MIECs. It was shown that these relations depend crucially on the nature of the electrodes, whether blocking for ions or not. Another important factor that controls the $I_e - V$ relations is the energy gap, whether it is large to the extent that only one electronic specie prevails or it is small so that both electrons and holes may exist, though under different oxidation conditions. In the first case a limiting current is obtained when both electrodes are ion blocking. In the second case the $I_e - V$ relations diverge with V . Other properties of the MIEC have a minor effect on these relations and do not alter them qualitatively. Results of $I_e - V$ measured

on Cu₂O, which corresponds to one defect model, under ion blocking electrodes, are presented and analyzed in terms of the theory discussed before.

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