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Modeling and potential measurements on light-emitting electrochemical cells

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1 Introduction
1.1 Light-emitting electrochemical cells
1.1.1 Introduction

Modern electronics based on organic semiconductors is a flourishing technology because of its low-cost, simple processing and high efficiency. Electroluminescent devices based on these semiconductors have received lots of attention since Tang and VanSlyke presented the first organic light emitting diode (OLED) to the world in their paper in 1987\(^1\). Now, more than 20 years later, OLED displays are being incorporated in televisions and mobile phones.

In its shadow an alternative organic light emitting device was discovered by Pei \textit{et al.} in 1995: the light-emitting electrochemical cell (LEC)\(^2\). This device is similar in structure to OLEDs with the only exception that ions are incorporated in its active layer, creating positive and negative changes in the device performance. Its resultant relative insensitivity to electrode material and interelectrode distance made this device very promising to overtake OLED technology. However, its short life-time as well as an inadequate understanding of the physics and chemistry behind its operation has limited the interest of academia and the industry as of today.

Still, extensive research has been done on these devices so far. Two dissimilar models have been proposed, both based on different observed aspects of LECs: The electrochemical doping model\(^2,3,4\) predicting a significant part of the applied potential to drop over a p-n junction in the organic layer and the electrodynamic model\(^5,6,7,8\) predicting the entire applied potential to drop over electric double layers at the electrodes. Recently, potential measurements on planar LECs have proved the presence of a dynamic organic p-n junction\(^3\), indicating that the LEC operation is electrochemical in nature.

Up till now however, no results from numerical studies have been published, demonstrating that the transient and steady-state behavior of a complete LEC are described by the electrochemical doping model. In contrast, such results have been reported by deMello \textit{et al.} supporting the electrodynamic model\(^5,6,7\). Therefore, this project focuses on the development and use of a numerical model to study the processes occurring in LECs during operation in order to obtain an increased understanding of its functioning. The modeling is complemented by several experimental techniques, \textit{e.g.} potential measurements on real, operating LECs and visualization of electrochemical doping via UV-excited photoluminescence.
1.1.2 Principle

Organic light emitting devices, e.g. OLEDs or LECs, consist of an organic semiconductor sandwiched in between two electrodes. This organic semiconductor either is a conjugated polymer or a small molecular material. The energy levels in these materials are filled by electrons in such a way that there is an energy gap $E_g$ in between the highest filled and lowest unfilled energy level. In polymers, these energy levels are called the HOMO, highest occupied molecular orbital, and LUMO, lowest unoccupied molecular orbital. For devices in operation, these energy levels are mainly used for transport of electrons and holes (absent electrons) after injection from the electrodes into the semiconductor.

A typical energy level diagram of a monolayer OLED is shown in Figure 1. Here $E_F$ is the Fermi level of the electrodes, which depends on the type of electrode material, and $\Phi_n$ and $\Phi_p$ are the injection barriers for electrons and holes respectively due to mismatch between the semiconductor transport and electrode Fermi levels. For OLEDs the injection barrier should not be larger than a few tenths of an eV so that the current density through the device is not limited by injection. Such small injection barriers can be facilitated by addition of injection layers next to the emitting layer. When a sufficient bias voltage $V_{bias}$ is applied, electrons and holes are injected and move in opposite directions due to the external electric field. Electrons and holes attract each other, forming electron-hole pairs called excitons. In organic materials, the binding energy of these excitons is relatively large (~0.5 eV), which makes the chance of exciton dissociation relatively small in organic LEDs compared to inorganic LEDs. Part of these excitons recombines while emitting a photon with an energy corresponding to $E_g$.

![Figure 1 | Energy level diagram of an OLED.](image)

Unlike OLEDs, LECs have mobile ions incorporated in the active layer. The exact role of these ions is still under debate and the two models trying to predict this are discussed in the next paragraph. The ions, e.g. lithium trifluoromethanesulfonate (LiCF$_3$SO$_3$) as was used in the very first LEC by Pei et al., are implemented in the device by mixing them with light emitting polymer (LEP) before deposition of the layer. The solid electrolyte Poly(ethylene oxide), PEO, is added as well to this mixture to improve the mobility of the ions. Other types of LECs exist as well, e.g. ones that consist of only one component: an ion transition metal complex (iTMC), such as ruthenium tris-
bipyridine hexafluorophosphate, \([\text{Ru(bpy)}_3]^{2+}(\text{PF}_6^-)_2\)\(^8,9\). In these devices, the complex carries out all three necessary tasks: 1) the decrease of the injection barriers, 2) the transportation of the electrons and holes and 3) the generation of excitons that emit light via phosphorescence.

### 1.1.3 Two models

The field of research of LECs has been dominated by two distinct models that predict the LEC device physics: the electrochemical doping model (ECD) and the electrodynamic model (ED). These models are best distinguished by the steady-state potential profile in sufficiently biased LECs (\(V_{\text{bias}} > E_g\)): The ECD states that a p-n junction is formed over which a significant amount of the applied potential drops (see Figure 2i), while the ED assumes the potential to mainly drop at thin layers near the electrodes, leaving the bulk nearly field-free (see Figure 2j).

In Figure 2 the processes leading to these different final states are illustrated for the ECD (see Figure 2a-d) and the ED (see Figure 2e-h). The ECD predicts that initially (a), in the unbiased state, only paired ions are present in the bulk, distributed homogeneously. Then, after application of a bias (\(V_{\text{bias}} > E_g\), anions and cations start moving in opposite directions. The ions are blocked by the electrodes, where they form EDLs (see Figure 2b). Subsequently, when the potential drop over the EDLs has become large enough with respect to \(\Phi_n\) and \(\Phi_p\), ohmic contacts are formed resulting in injection of electrons and holes. The buildup of bulk space charge by the enhanced injection of electronic charge carriers is minimized by the response of the anions and cations. Anions (cations) move away from the electron (hole) injecting contact. Hence, regions are formed in which electrons (holes) are electrostatically compensated by cations (anions). Because of the similarity to the (static) situation encountered in doped inorganic semiconductors, this process is commonly referred to as (electrochemical) doping of the conjugated polymer (see Figure 2c). Finally, in steady-state, the anions and cations have become spatially separated, whereas the total ion current vanishes\(^10\). At the same time, electrons and holes recombine at the p-n junction formed in the centre (see Figure 2d).

During LEC operation as predicted by the ED, the first two steps are the same (see Figure 2e and f). However, after injection of charge carriers has initiated, the ions continue to move towards the electrodes (see Figure 2g) until finally the most significant part of \(V_{\text{bias}}\) drops near the electrode interfaces and the bulk becomes field-free (see Figure 2h). No distinct doping of the polymer in the bulk of the device is assumed.

Both these models have been supported by experimental results\(^4,5,11\). Measurements of the potential profile in planar surface cells have provided evidence for both models. Slinker et al.\(^8\) have shown with electric force microscopy that the applied potential drops mainly close to the electrode interfaces. Later on, Maturova et al.\(^3\) proved that a dynamic p-n junction can form in the bulk of the active material from which light is emitted. Electrochemical doping however, advocated only by the ECD, has been visualized in planar LECs under UV-illumination by monitoring the doping-induced quenching of photoluminescence (PL)\(^4,11\). Also modeling studies favoring the ED\(^5,6,7,8\) as well as the ECD have been published\(^12,13,10\).
Figure 2 | Schematic illustrating the electrochemical doping model (a-d and i) and the electrodynamic model (e-h and j). a and e, Homogeneous ion distribution in unbiased devices. For the electrochemical doping model: b, formation of EDLs, c, injection of charge carriers and resultant doping of the polymer and d, recombination in the then formed p-n junction. For the electrodynamic doping model: f, formation of EDLs, g, injection of charge carriers and continued formation of EDLs and h, recombination. i and j, The transient potential profiles with the final state in red.
1.2 Numerical model

1.2.1 Principle

In order to describe the device operation of the LEC, a 1-dimensional model was used. This model describes the LEC as an OLED containing ions. Furthermore, no binding energy is assumed between the anions and cations, so the only attractive interaction between both is electrostatic in nature. The electronic and ionic mobility is assumed not to be field-dependent. The active layer is trap-free, has length $L$, is divided in $N$ equidistant grid-points and has a single well-defined energy gap $E_g$. In real polymers a distribution of energy gaps is present due to disorder, which is ignored in this model. The anode is positioned at $x = 0$ and the cathode at $x = L$. An energy level diagram of the modeled LEC is shown in Figure 3. For the injection mechanism a modified expression of Boltzmann’s law was used: the ‘modified Boltzmann’ injection law. The main advantage of this law is a reduced simulation time. The precise mechanism of injection has no effect on the simulation results. By changing the injection model, the rate of carrier injection can be controlled to study its effect on the device operation. The justification of this injection law as well as a comparison with other injection laws is discussed in chapter 3 and Appendix 7.3. In the modified Boltzmann injection model we used a Boltzmann factor to describe injection in the following manner taking into account the band bending just behind the first grid-point:

$$n (1) = \exp \left( -\frac{\Phi_n + [V(2) - V(1)]}{kT} \right)$$

(1)

for electrons and

$$n (1) = \exp \left( -\frac{\Phi_p - [V(2) - V(1)]}{kT} \right)$$

(2)

for holes, where $n(1)$ and $p(1)$ are the respective electron and hole density on grid-point 1; $V(1)$ and $V(2)$ are the potentials at grid-points 1 and 2 respectively; $k$ is Boltzmann’s constant and $T$ the temperature. Hence, the Boltzmann factor is effectively evaluated at the 2nd grid point. In addition, in this model injection is not affected by the grid-point spacing and thus longer devices can be simulated while not having to alter the amount of grid-points because of injection problems.

At the positive and negative electrode, Boltzmann equilibrium is maintained for the electrons and holes respectively. Bulk transport of electrons and ions is described by the following drift and diffusion equations:
\[ J_n = n q \mu_n \frac{dV}{dx} + k T \mu_n \frac{dn}{dx}, \quad (3) \]
\[ J_p = p q \mu_p \frac{dV}{dx} - k T \mu_p \frac{dp}{dx}, \quad (4) \]
\[ J_a = a q \mu_a \frac{dV}{dx} + k T \mu_a \frac{da}{dx}, \quad (5) \]
\[ J_h = c q \mu_c \frac{dV}{dx} - k T \mu_c \frac{dc}{dx}, \quad (6) \]

where \( J \) and \( \mu \) refer to the current density and mobility of the charge carriers; \( n, p, a \) and \( c \) refer to electron, hole, anion and cation density respectively and as well denote the type of charge carrier when used as subscript. \( q \) is the absolute electronic charge and \( V \) the potential. Einstein’s relation between the diffusion constant and the mobility is assumed to apply. The ion current is zero at the electrodes, for the electrodes are ionically blocking. The electrons and holes recombine following a Langevin process:
\[ R = \frac{q (\mu_n + \mu_p)}{\varepsilon_0 \varepsilon_r} p n, \quad (7) \]

where \( R \) is the recombination rate; \( \varepsilon_0 \) and \( \varepsilon_r \) are the dielectric and the relative dielectric constant respectively. The continuity equations are
\[ \frac{dn}{dt} = \frac{1}{q} \frac{dJ_n}{dx} - R \quad (8) \]
for electrons and
\[ \frac{dp}{dt} = - \frac{1}{q} \frac{dJ_p}{dx} - R \quad (9) \]
for holes. The potential profile throughout the device is calculated by Poisson’s equation:
\[ \nabla^2 V = - \frac{q}{\varepsilon_0 \varepsilon_r} (p - n + c - a). \quad (10) \]

Initially, the LEC contains neither electrons nor holes, but only has a constant ion concentration. Therefore, the electric field throughout the device is constant at the start. The model then uses equations (1) – (10) and the given boundary conditions to calculate the necessary quantities, e.g. carrier concentrations, current densities and potentials, starting from the first grid point until the last grid point. This process is reiterated for user-defined time steps forward in time.

In the following paragraphs, simulation results are shown of an LEC with the following specifications: \( c_0 = \langle a \rangle = \langle c \rangle = 0.1 \text{ nm}^{-3}, \ g_0 = 0.3 \text{ nm}^{-3}, \ E_g = 2 \text{V}, \) equal electrodes were used with \( \Phi_e = 1.5 \text{ eV} \) and \( \Phi_h = 0.5 \text{ eV}, \ V_{\text{bias}} = 5 \text{V}, L = 2 \mu\text{m}, N = 41, T = 300 \text{ K}, \mu_a = \mu_c = \)
5·10^{11} \text{ m}^2\text{V}^{-1}\text{s}^{-1} \text{ and a doping dependent } \mu_p = \mu_n \text{ was used starting at } 5·10^{11} \text{ m}^2\text{V}^{-1}\text{s}^{-1} \text{ at zero doping and } 5·10^{-9} \text{ m}^2\text{V}^{-1}\text{s}^{-1} \text{ at maximum doping (see paragraph 2.2 for a detailed description of this doping dependence).}

1.2.2 Electric double layer formation

The modeling results of an LEC during operation at 5V from \( t = 0 \) until the EDLs have completely formed are shown in Figure 4. Here, \( \rho \) refers to the charge density.

![Figure 4](image_url)

**Figure 4 | Results of the response of the modeled LEC just after application of 5V.** The order of measurements is from light gray towards black where the final result is red. **a**, The transient potential profile. The blue arrows accentuate the movement of the graphs in time. **b**, The transient difference between the density of positive and negative particles throughout the device. The two black arrows point at the charge carrier density causing the increased potential drop shown at the interfaces (a). **c** and **d**, The transient anion (circles) and cation (stars) concentration near the anode and cathode respectively. The numbered arrows indicate the position where the anion and cation concentrations start to differ. The numbers correspond to \( t = 2·10^{-7}, 2·10^{-4}, 8·10^{-4} \) and \( 14·10^{-4} \text{ s} \) respectively for 1 to 4.

Relatively large electric fields arise at the electrode interfaces (see Figure 4a) due to space charge being piled up near the electrodes which is pointed out in Figure 4b. The arrows here indicate the amount of charge carriers responsible for these enhanced electric
fields, which are situated on grid points 2 and \(N\)-1. Note the large amount of net charge carriers at the grid points 1 and \(N\) \((x = 0\) and 2000 nm respectively, which are beyond the range of the graph). These charge carriers do not contribute to the observed potential profile due to boundary conditions at the first and last grid-point: \(V(x = 0) = V_{bias}\) and \(V(x = L) = 0\). Thus these charge carriers do not contribute to injection enhancement. This effect can be justified by the image potential in the metal effectively screening the charge of ions close to the electrodes.

These large amounts of charge carriers, \textit{i.e.} anions and cations at the anode and cathode respectively, are needed to maintain the smaller amounts of these same charge carriers at grid points 2 and \(N\)-1 following a drift-diffusion equilibrium.

A close view on the ion concentrations near the electrodes is shown in Figure 4c and d. Initially (light gray lines) the ion concentration is equal anywhere in the device. After some time however, the anions and cations start moving in opposite directions due to the applied electric field. Hence, the anions and cations are depleted or piled up at the edges as shown in Figure 4c and d. Consequently, space charge is being formed near the contacts until the resultant electric field is strong enough so that finally the injection of electrons and holes is initialized.

\subsection*{1.2.3 Doping fronts}

After the EDLs have been formed, injection of electrons and holes is initiated. Anions and cations then pair with these holes and electrons respectively to compensate for their charges, \textit{i.e.} dope the active layer. The modeling results after EDL formation until the electrons and holes have met are shown in Figure 5.

In Figure 5c fronts of electrons and holes are observed moving towards each other until they collide. After the fronts have met, recombination is initiated as shown in Figure 5b. The response of the ions is shown in Figure 5d and Figure 5f, clearly indicating that the anions and cations redistribute in order to compensate the electric charges of the electrons and holes. The net charge carrier density is shown in Figure 5e, corresponding to the potential profiles in Figure 5a. At the electrodes there is a large total charge density originating from ions to enhance injection of electrons and holes. At the position of the doping fronts also a net charge density is observed due to electrons and holes that have not yet paired with cations or anions respectively.

When the fronts have met, still anions and cations are present in both doped regions. Furthermore, also no p-n junction is observed in the potential profile.
Figure 5 | Results of the response of the modeled LEC to the application of 5V after EDL formation. The order of measurements is from light gray towards black with the final result in red. Additional blue arrows are added accentuating the movement of the graphs during the time evolution. a, Transient potential profile, b, transient recombination rate distribution, c, transient electronic charge carrier distribution, d, transient ion distribution, e, transient net charge carrier density distribution and f, the difference between the cation and anion density.
1.2.4 P-n junction formation

In LECs, one condition of steady-state due to the ion-blocking electrodes is a resultant zero ion current. After the fronts had met as shown in Figure 5, still a total nonzero ion current was calculated. This current consisted of anions and cations moving away from the n-doped and p-doped areas respectively to increase doping on the other side. After continuation of the simulations, the anions and cations ultimately became completely

Figure 6 | Results of the response of the modeled LEC to application of 5V after fronts have already met. The order of measurements is from light gray towards black with the final result in red. Additional blue arrows are added accentuating the movement of the graphs during the time evolution. a, Transient potential profile, b, transient recombination rate distribution, c, transient electronic charge carrier distribution, d, transient ion distribution, e, transient net charge carrier density distribution and f, the difference between the cation and anion density.
separated so that an intrinsic region arose in between the doped areas. Due to the larger resistance, a large part of the potential dropped over this region, forming a p-n junction. The evolution of the potential, the charge carrier concentrations and the recombination profile is shown in Figure 6.

Steady-state was not yet reached because of extremely long calculation times needed. Therefore cations are still present in the p-doped area, slowly moving towards the n-doped region. However, it is evident that the p-n junction has formed relatively close to the electrode with the largest injection barrier. Due to the larger EDL there, fewer ions are available to n-dope the polymer compared to the p-doping on the other side. The cations still present in the p-doped region will however likely push the p-n junction more to the centre.

The results show that the numerical model evolves as is predicted by the ECD for the specified initial conditions.
1.3 Experimental Techniques

To provide experimental evidence to complement the modeling done on LECs, several experimental techniques were employed to characterize different properties of LECs during operation. To probe the local electrostatic potential of LECs with a large interelectrode gap, scanning Kelving probe microscopy (SKPM) is used. On these same devices, optical characterization can be performed as well to provide information about doping in the active layer. First however, the preparation of 3-component LECs is explicated.

1.3.1 Sample preparation

For the fabrication of devices, one of the following two conjugated polymers was used: poly[2-methoxy-5-(3’,7’-dimethyloctyloxy)-p-phenylenevinylene] (MDMO-PPV, $M_w > 1 \times 10^6$ g mol$^{-1}$, American Dye Source) or phenyl-substituted poly(p-phenylene vinylene) copolymer (SY-PPV, $M_w = 2 \times 10^6$ g mol$^{-1}$, Merck, catalogue number PDY-132). Poly(ethylene oxide) (PEO, $M_w = 5 \times 10^5$ g mol$^{-1}$, Aldrich) was used as received and the salt potassium trifluoromethanesulfonate (KCF$_3$SO$_3$ or KTf, 98 %, Aldrich) was first dried at 473 K under vacuum before use. The conjugated polymer (CP) SY-PPV was dissolved in cyclohexanone (> 99 %, anhydrous, Aldrich) at a concentration of 5 mg/ml, and the CP MDMO-PPV was dissolved in chloroform (> 99.8 %, anhydrous, Aldrich) at a concentration of 10 mg/ml. PEO and KCF$_3$SO$_3$ were dissolved separately in cyclohexanone (> 99 %, anhydrous, Aldrich) both at 10 mg/ml concentrations. These solutions were mixed together in a mass ratio of CP: PEO: KCF$_3$SO$_3$ = 1:1.35:0.25. This blend solution was thereafter stirred on a magnetic hot plate at $T = 323$ K for 5 h. Glass substrates ($1 \times 1$ cm$^2$) or ITO precovered glass substrates were cleaned by subsequent ultrasonic treatment in detergent, distilled water, acetone and isopropanol.

The substrates were spin-coated with the blend solution (at 800 rpm for 60 s, followed by 1000 rpm for 10 s) after which they were dried at $T = 323$ K for at least 1 h on a hot plate. The thickness of the film was ~250 nm, as determined by profilometry.

![Figure 7](image)

Figure 7 | Schematic diagram of the device configurations. a, planar cell configuration. b, Sandwich cell configuration. The mixture consists of a conjugated polymer, i.e. MDMO-PPV or SY-PPV, PEO and KCF$_3$SO$_3$.

After deposition of the organic layer Al or Au electrodes were deposited by thermal evaporation under high vacuum ($p \approx 1 \times 10^{-6}$ mbar). A thin wire-based shadow mask was used to create an inter-electrode gap of approximately 100 µm to fabricate
planar cells. An illustration of the device layout is shown in Figure 7. All of the above mentioned procedures, save for the cleaning of the substrates and the evaporation of the electrodes, were done in a glove box under N\textsubscript{2} atmosphere ([O\textsubscript{2}] < 1 ppm and [H\textsubscript{2}O] < 1 ppm).

1.3.2 Scanning Kelvin Probe Microscopy

In scanning Kelvin probe microscopy, the surface potential of a sample is measured by adjusting the potential of the tip in order to minimize the electric force on the tip due to the potential of the sample. Minimization is achieved when the potential of the sample and the tip are equal.

To measure the surface potential, an oscillating voltage $V_{AC} \sin \omega t$ is applied to the tip, where $V_{AC}$ is the amplitude of the oscillation and $\omega$ the resonant frequency of the cantilever. The energy in a parallel plate capacitor $U$ can be used as a start to describe the response of the tip on the sample:

$$U = \frac{1}{2}C(\Delta V)^2,$$  

where $C$ is the local capacitance between the tip and sample and $\Delta V$ the potential difference between both. The force $F$ on the tip is

$$F = -\frac{dU}{dz} = -\frac{1}{2} \frac{dC}{dz}(\Delta V)^2,$$  

where $z$ is the distance between the tip and the sample. The potential difference consists of a DC and AC component:

$$\Delta V = \Delta V_{DC} + V_{AC} \sin \omega t.$$  

Here $\Delta V_{DC}$ refers to the potential difference between the tip and the sample, which includes most importantly work function differences, surface charge effects and the applied DC voltage between tip and sample.

Filling in equation (13) in equation (12), one obtains for the force $F$ on the tip:

$$F = -\frac{1}{2} \frac{dC}{dz} \left(\Delta V_{DC}^2 + \frac{1}{2}V_{AC}^2\right) - \frac{dC}{dz} \Delta V_{DC} \cdot V_{AC} \sin \omega t + \frac{1}{4} \frac{dC}{dz} V_{AC}^2 \cos 2\omega t.$$  

Here, only the second term has a frequency equal to the resonance frequency of the tip. The tip responds mainly to forces at its resonance frequency, so the first term (DC) and the third term (at $f = 2\omega$) do not result in any significant effect on the tip oscillation. If now $\Delta V_{DC} \neq 0$, then there is a non-zero oscillating force on the tip. Altering the bias voltage on the tip such that $\Delta V_{DC} = 0$, results in a oscillating force equal to zero, stopping the tip oscillation. The latter can be detected in order to locally determine the potential on the sample surface. The resolution is approximately 100 nm, which is relatively small as compared to the features studied in this research.
1.3.3 Optical probing

Electro-optical probing under UV-light of LECs opens up the opportunity to indicate doping formation in the active layer via doping-induced quenching of the UV-excited photoluminescence. Furthermore, also the light emission can be mapped with this technique.

Optical probing is performed in an optical-access cryostat under high vacuum \((p < 10^{-5} \text{ mbar})\), using a single-lens reflex camera (Canon EOS50) equipped with a macro lens (focal length: 65 mm) and a teleconverter \((\times 2)\). In parallel with the optical probing, the current can be measured with a computer-controlled source-measure unit (Keithley 2612).
1.4 Outline of the thesis

The possibility of using experimental techniques alongside a numerical model opens up the opportunity to study complex, underlying mechanisms hidden behind experimental observations. In LECs, such a study is of great importance, since a lot of experimental data has been gathered, not resulting in a consensus regarding the fundamental device physics.

In this thesis, both transient and steady-state characteristics of LECs are considered. Regarding the transient characteristics, studies on LECs by UV-excited PL have shown that doping fronts arise in LECs after application of a sufficient bias voltage. In chapter 2, the underlying mechanism of these doping fronts is studied numerically. Specifically, the doping dependence of the electron/hole mobility is found to be crucial for both the formation and acceleration of doping fronts.

In chapter 3, the focus lies on the operation of LECs in steady-state. Here, two seemingly physically distinct device models are unified by combination of experimental observations with numerical calculations: both models exist in different injection rate regimes. Furthermore, the drift and diffusion contributions to the steady-state current are studied and shown to differ as well in these different regimes. From this study, also a $I(V)$ curve was analytically determined, verified by the numerical model.

In the final chapter, the effect of a reduced ion concentration on both the transient and steady-state characteristics is investigated. It is shown that the total current density is significantly reduced, leading to several effects, *e.g.* a broadened p-n junction, reduced EDLs and decreased doping.
2 Modeling of transient behavior in LECs

2.1 Introduction

One of the appealing properties of LECs is their relative insensitivity to the interelectrode distance. This creates possibilities to engineer devices with a millimeter-sized gap, which allows for characterization of transient and steady-state properties that are impossible to monitor for techniques at hand in devices with an active layer thickness of the order of hundreds of nanometers.

Gao et al.\textsuperscript{4} first introduced results of UV-excited photoluminescence on LECs in which doping front propagation was observed. Two fronts, one n-type and the other p-type, could be observed due to the photoluminescence being quenched by doping of the polymer. A study of these doping fronts revealed an acceleration in their movement towards each other. To describe this motion Robinson et al.\textsuperscript{11} derived the following expression for the time dependence $t$ of the p-doping front position $x_p$ in LECs:

$$x_p = \frac{1}{1 + \frac{\gamma_p}{\gamma_n}} \left[ 1 - 2V_i \sigma_i \left( \frac{1}{\gamma_n} + \frac{1}{\gamma_p} \right) t \right]^{1/2},$$

(15)

with $V_i$ the potential over and $\sigma_i$ the ionic conductivity in the intrinsic region of the polymer. $\gamma_n$ and $\gamma_p$ represent the charge density required to n- and p-dope the polymer respectively. Assumptions are that the polymer is doped uniformly and that both $V_i$ and $\sigma_i$ are constant. A similar expression exists for the n-doping front position $x_n$. The observed acceleration of the doping fronts is expected to be due to an increase of the electric field when the fronts close in on each other. This increase is the result of a decrease of the distance between the fronts and a constant $V_i$.

Other measurements done on these planar LECs are current versus time and light emission versus time measurements\textsuperscript{5,14}. After application of a bias voltage, a non-zero and decreasing current is measured. For unipolar devices this continues until steady-state is reached and a constant, non-zero current is measured. For bipolar devices the current rises strongly after a certain period of time. At some point during this increase, the initiation of light emission is observed. No results have yet been published confirming the presence of a p-n junction at the same time. After this initiation of light emission, the current continues to rise followed by a relatively strong decrease. The origin of this decrease is alleged to be due to chemical side reactions\textsuperscript{14}. Others\textsuperscript{5} however, favoring the electrodynamic model (ED) over the electrochemical doping model (ECD), have proposed that this decrease of the current density originates from the strong reduction of the bulk potential due to the redistribution of the ions. Consequently, the drift current of the mobile charge carriers should be strongly reduced, which could explain the observed current drop.

In this chapter, a model, describing the processes occurring in LECs, was used to determine the origin of the accelerating doping fronts as well as the processes underlying
the measured transient current and light emission curves of LECs. The former is expected to be due to a doping dependent electron and hole mobility, $\mu_n$ and $\mu_p$ respectively. Strong doping dependence of the mobility has been experimentally observed by Shimotani et al.\textsuperscript{15} They showed that the enhancement of the carrier mobility due to electrochemical doping is significantly larger than the enhancement due to field-effect doping.

### 2.2 Methods

The model described in chapter 1.2 was used to study the transient processes occurring in LECs.

The LEC that was simulated has a thickness of 2000 nm divided over 41 grid points. A semiconductor with a 2 eV bandgap and relative dielectric constant $\varepsilon_r = 3$ was used, sandwiched in between two equal work function metals so that $\Phi_e = 1.5$ eV and $\Phi_h = 0.5$ eV. The density of states of the highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO, of the semiconductor, $g_0$, was set at 0.3 nm\textsuperscript{-3} and the average ion concentration $c_0 = \langle a \rangle = \langle c \rangle = 0.1$ nm\textsuperscript{-3}. A bias voltage of 5 V was applied to these electrodes at $t = 0$ and temperature $T = 300$ K. Furthermore, the ion mobility $\mu_{ion} = \mu_a = \mu_e$ as well as $\mu_{p/h} = \mu_n = \mu_p$. In case of a doping independent electron and hole mobility, the mobility was set at $5 \cdot 10^{-11}$ m\textsuperscript{2} V\textsuperscript{-1}s\textsuperscript{-1}. For simulations in which a doping dependent mobility was required, a mobility curve $\mu(occ)$ was parameterized as follows (also see Figure 8):

$$
\mu(occ) = (\mu_e - \mu_0) \cdot \frac{\exp\left(\frac{occ - occ_0}{W}\right)}{1 + \exp\left(\frac{occ - occ_0}{W}\right)} + \mu_0. 
$$

Here $occ$ refers to the doping fraction which is equivalent to the density of electrons or holes for n-type and p-type doping respectively: $occ = n/g_0$ and $occ = p/g_0$ for n- and p-type doping respectively. Note that the polymer is completely doped, i.e. $occ = 1$, when $g_0$ is completely filled: $n = g_0$ or $p = g_0$. $\mu_0$ and $\mu_e$ refer to the mobility at doping fractions of 0 and 1 respectively. $W$ and $occ_0$ are constants which determine the range of doping fractions at which the mobility changes from $\mu_0$ to $\mu_e$. This curve is similar in shape to the curve experimentally obtained by Shimotani et al.\textsuperscript{15}.

![Figure 8](image_url)
2.3 Results and Discussion

2.3.1 Formation of doping fronts

Simulations were performed for values of $\mu_{\text{ion}}$ ranging from $5 \cdot 10^{-12}$ to $5 \cdot 10^{-9}$ m$^2$V$^{-1}$s$^{-1}$ for both doping dependent ($\mu_{n,0} = \mu_{p,0} = 5 \cdot 10^{-11}$ m$^2$V$^{-1}$s$^{-1}$ and $\mu_{n,\infty} = \mu_{p,\infty} = 5 \cdot 10^{-9}$ m$^2$V$^{-1}$s$^{-1}$) and independent ($\mu_p = \mu_n = 5 \cdot 10^{-11}$ m$^2$V$^{-1}$s$^{-1}$). Other relevant parameters were: $c_0 = \langle a \rangle = \langle c \rangle = 0.1$ nm$^{-3}$, $g_0 = 0.3$ nm$^{-3}$, $E_g = 2$ eV, $\Phi_e = 1.5$ eV and $\Phi_h = 0.5$ eV, $L = 2000$ nm, $N = 41$ and $T = 300$ K. The resultant time-evolution of the carrier concentration profiles throughout these devices just after application of $V_{\text{bias}} = 5$V are shown in Figure 9.
Figure 9 | Transient carrier concentration profiles in LECs. a-d. Profiles for a constant $\mu_{pn}$. e-h. Profiles for a doping dependent $\mu_{pn}$. Holes (stars) are injected from the left electrode and electrons (circles) from the right electrode. The corresponding values of $\mu_{on}$ are shown at the top of each graph expressed in $m^2 V^{-1} s^{-1}$. 

2-20
Initially, just after application of 5 V, the processes occurring in all simulated devices are similar: the ions move towards the electrodes forming EDLs. Consequently electrons and holes are injected and start moving towards the opposite side of the LEC. After this the processes in the devices differ. In order to interpret these results, the discussion is centered on the following characteristics: The moment at which recombination starts, i.e. the electron and hole fronts meet each other, and the saturation of the doping, which can be derived from the charge carrier concentration at each grid point.

In case $\mu_{\text{ion}} = 5 \cdot 10^{-12} \text{m}^2\text{V}^{-1}\text{s}^{-1}$, the electrons and holes meet before the doping level is saturated for both doping dependent and independent $\mu_{\text{p/n}}$. This is due to the electrons and holes always being faster than the ions. Resultantly, the doping level increases more or less uniformly in time in the doped regions and no clear doping fronts are observed.

In case $\mu_{\text{ion}} = 5 \cdot 10^{-11} \text{m}^2\text{V}^{-1}\text{s}^{-1}$, a similar result is observed for constant $\mu_{\text{p/n}}$. However, because the ion mobility is increased by a factor 10, they can keep up better with the relatively fast moving electrons and holes. The result is that saturation takes place relatively fast. Nonetheless, still no pronounced doping fronts are observed. For doping dependent $\mu_{\text{p/n}}$ fronts are observed: regions with a nearly constant electron and hole concentration are found moving from the electrodes towards each other. The formation of the fronts here is due to the electrons and holes having an increased mobility in the doped areas. As a result, the electrons and holes behind the fronts are faster than the ions and thus move towards the fronts, while the carriers at the fronts are not able to keep ahead. So saturation of the doping already occurs before the fronts have met, which is observed as doping fronts.

In case $\mu_{\text{ion}} = 5 \cdot 10^{-10} \text{m}^2\text{V}^{-1}\text{s}^{-1}$, doping fronts are observed for both constant and doping dependent $\mu_{\text{p/n}}$. The origin of these fronts are however slightly different. For constant $\mu_{\text{p/n}}$, the ions move much faster than the mobile charge carriers. The result is that the ions pile up at the electrodes well before the electrons and holes have moved into the semiconductor: Note the increased electron and hole concentrations close to the electrodes. As a result the ions screen the electric field in the bulk and thus reduce the driving force behind the movement of the electrons and holes into the LEC. Consequently saturation takes place before the electron and holes meet, which leads to the formation of doping fronts moving towards each other. In case of a doping dependent $\mu_{\text{p/n}}$, the result is similar to the case where $\mu_{\text{ion}} = 5 \cdot 10^{-11} \text{m}^2\text{V}^{-1}\text{s}^{-1}$. The only difference is that mainly at the electrode with the largest injection barrier, i.e. the cathode in this case, the ions pile up well before the fronts have formed and started to move towards each other.

In case $\mu_{\text{ion}} = 5 \cdot 10^{-9} \text{m}^2\text{V}^{-1}\text{s}^{-1}$, doping fronts are observed as well and the LECs behave similar to the case $\mu_{\text{ion}} = 5 \cdot 10^{-10} \text{m}^2\text{V}^{-1}\text{s}^{-1}$ where the effects due to faster ions are more pronounced now.

### 2.3.2 Doping front speed

Experimental results published by Gao et al.\textsuperscript{4} demonstrated that in planar LECs doping fronts are observed by UV-excited photoluminescence. These fronts accelerated when closing in on each other, as demonstrated analytically and experimentally by Robinson et al.\textsuperscript{11}. For the simulated results shown in the previous paragraph, the front position versus
time was plotted (see Figure 10), only in case fronts were observed. The front position is determined by the position where the doping concentration is equal to a certain value, approximately 3 orders below $g_0$.

![Graph showing simulated front position for LECs with different $\mu_{\text{ion}}$ and $\mu_{\text{p/n}}$.](image)

**Figure 10 | Simulated front position for LECs with different $\mu_{\text{ion}}$ and $\mu_{\text{p/n}}$.** Holes and electrons are denoted by stars and circles respectively. The inset shows the corresponding absolute values of the front speed. The vertical axis is logarithmic, whereas the horizontal axis is linear.

The following observations can be obtained from these results: For increasing $\mu_{\text{ion}}$, both the onset of carrier injection and the meeting of the doping fronts occur earlier. The former can be attributed to the ions forming their respective EDLs faster due to increased conductivity. The latter is due to the more mobile ions being more able to accompany and react to the electrons and holes that enter the organic layer. This effectively raises the front speed.

In the previous paragraph, it was observed that in case of $\mu_{\text{ion}}$ is larger than $\mu_{\text{p/n}}$, the ions screen the bulk electric field. This screening decreases the driving force of the movement of the doping fronts of which the effect is observed in Figure 10: In case of relatively large $\mu_{\text{ion}}$, the front speed declines when penetrating more in the bulk. Only in case $\mu_{\text{p/n}}$ is larger than $\mu_{\text{ion}}$, e.g. the dark red curve in Figure 10, the electrons and holes can prevent this deceleration and even accomplish a small acceleration of the doping fronts. This effect is less pronounced in the dark blue curve, because here $\mu_{\text{ion}}$ is a factor 10 larger: The front speed is more or less constant. This effect is also observed when comparing the doping dependent results with the doping independent ones: For doping dependent $\mu_{\text{p/n}}$ the fronts have a larger front speed and a smaller deceleration due to increased mobility in the doped areas.
Other simulations were done on similar LECs with altered doping dependent $\mu_{p/n}$ curves and for different $c_0$.

The doping dependence of $\mu_{p/n}$ was altered in such a way that the rise in mobility occurred less gradual for increasing doping fraction as shown in Figure 11b. The mobility curve denoted by $W = 0.04$ is the one used in the simulation of which the result is the dark red curve shown in Figure 10. Also a mobility curve (Figure 11b orange curve) was used that is more similar in shape if compared with the results published by Shimotani et al.\textsuperscript{15}. The results of these simulations are shown in Figure 11.

![Figure 11 | Front position vs. time plots for different doping dependent mobility functions.](image)

The simulations demonstrate that a sudden increase of $\mu_{p/n}$ results in the fronts meeting each other more rapidly. Furthermore, the acceleration of the fronts increases as well.

The results of simulations of LECs with different initial ion concentrations are shown in Figure 12.
The results clearly indicate an increase of the front speed as well as a larger acceleration of the fronts for increasing initial ion concentration. This increase can be attributed to an increase of ions at the EDLs and the doped areas. The former enhances mobile charge carrier injection whereas the latter effectively increases the doping fraction since more electrons and holes can be compensated by the ions.

The model derived by Robinson et al.\textsuperscript{11} which describes the front position versus time does not follow the here obtained results. From simulation results, it was observed that \( V_i \) and \( \sigma_i (\sim n_e(x) \text{ or } n_d(x)) \) were not constant during doping front propagation. See for more information Appendix 7.1. Therefore, the derived expression for the doping front position is not applicable in these simulations.

### 2.3.3 Transient current density and light emission

For the simulations described in paragraph 2.3.1 with \( \mu = \mu(\text{occ}) \), also the transient current density and recombination rate (\textit{i.e.} light emission) curves were recorded. The total current density \( J_{\text{total}} \), the ion current density \( J_{\text{ion}} \), the electron and hole current density \( J_{\text{p/n}} \) and recombination rate \( R \) for an LEC in operation with different \( \mu_{\text{ion}} \) are shown in Figure 13.
For all devices, starting at $t = 0\text{s}$, $J_{\text{total}}$ is carried completely by the ions, being the only type of charge carriers present inside the device at that moment. The ions form EDLs in the device which, when the EDL has become large enough, initiates injection of electrons and holes at some point. After this, the semiconductor becomes doped, which makes it possible for more mobile charge carriers to move through the device increasing $J_{\text{total}}$. This increase is due to the enhancement of $J_{\text{p/n}}$ by both an increase of the charge carrier density and $\mu_{\text{p/n}}$ due to doping. In case of relatively large $\mu_{\text{ion}}$, $J_{\text{total}}$ is increased relatively fast because doping occurs at a faster rate: The ions do not need much time to move to an electron or hole to form doping complexes.

The meeting of the doping fronts can be determined from the onset of recombination of charge carriers. A p-n junction however has not been formed yet in case $\mu_{\text{ion}}$ is relatively low, i.e. $5 \cdot 10^{-11}$ or $5 \cdot 10^{-12} \text{ m}^{2}\text{V}^{-1}\text{s}^{-1}$. For large $\mu_{\text{ion}}$ on the other hand, the p-n junction forms immediately when the fronts meet. The observed time delay of the p-n junction formation can be explained by the doping not being maximized yet in the doped regions. Consequently, the ions continue to move throughout the whole layer, including the junction region, in order to maximize doping. The junction however, can only form when no ions are present in the junction region because it has to be intrinsic. So therefore a time delay is observed. In case of relatively large $\mu_{\text{ion}}$, the ions have already been...

Figure 13 | $J$, $t$ and $R$, $t$ measurements on modeled LEC for different $\mu_{\text{ion}}$ and a doping dependent $\mu_{\text{p/n}}$ (c.f. Figure 9e-h). The blue, red, black and orange graphs represent the total current density $J_{\text{total}}$, the ion current density $J_{\text{ion}}$, the electron and hole current density $J_{\text{p/n}}$ and the recombination rate $R$ respectively. 1, 2, 3 and 4 refer to initiation of hole injection, initiation of electron injection, front meeting and p-n junction formation respectively.
separated before meeting of the fronts so that the intrinsic region is immediately formed after the fronts meet: A p-n junction is immediately formed (see e.g. Appendix 7.1 Figure S1d and h).

Another interesting characteristic of all graphs shown in Figure 13 is the sudden drop of $J_{p/n}$, $J_{ion}$, and $R$, which is observed when the p-n junction forms. The origin of this drop is discussed in chapter 3.5 and is related to the screening of the electric field in the doped areas by the ions: when the junction arises, the potential over the doped regions drops significantly (c.f. Figure 6a)

The four points that were marked in each graph of Figure 13 are shown together in Figure 14.

The time at which hole and electron injection are initiated, becomes approximately one order of magnitude larger each time $\mu_{ion}$ is enhanced by a factor 10. This result is expected because only the movement of the ions determine this onset time. The meeting of the fronts however does not show the same behavior. Starting from $\mu_{ion} = 5 \cdot 10^{-12}$, when $\mu_{ion}$ is enhanced by a factor 10, the meeting of the fronts goes faster, but not with the same factor 10. Obviously also the electrons and holes play a part in this process. At some point, an enhancement of $\mu_{ion}$ does not result in an earlier meeting of the fronts due to e.g. a strong screening effect caused by the ions that have already moved towards the interfaces (for more information see Appendix 7.1) or $\mu_{p/n}$ becoming a limiting factor. After this meeting, the p-n junction forms. At relatively large $\mu_{ion}$, the formation is limited by the meeting of fronts. However, the graph clearly shows that the ions have the largest contribution to the formation of the junction: for relatively low $\mu_{ion}$, an increase of the mobility from $5 \cdot 10^{-12}$ to $5 \cdot 10^{-11}$ results in faster junction formation by approximately a factor 10 as well. During the process of junction formation, mainly two processes occur: enhancement of the doping in the already doped areas and the removal of cations and anions from the p- and n-doped areas. The last process also limits the first because in
order to enhance doping, first unpaired ions must be supplied. This supply is the ion current throughout the device, which can be enhanced by e.g. increasing $\mu_{\text{ion}}$.

### 2.4 Conclusion

The formation of well-defined doping fronts is intimately related to the mobility of all charge carriers in the LEC: Saturation of the doping in the doped areas must be fast enough to keep up with the doping fronts moving towards each other. To establish this and to obtain accelerating doping fronts the following criteria can be set for the mobilities (see also Figure 15):

- $\mu_{\text{ion}}$ must be of the same order as $\mu_{\text{p/n}}$ in undoped areas.
- $\mu_{\text{p/n}}$ must be one or more orders larger than $\mu_{\text{ion}}$ in the doped areas.

Next to a doping dependent mobility, also the amount of ions available for doping ($\sim c_0$) is important to establish accelerating doping fronts. Due to more available ions, the doping fraction can be increased faster and to a higher level, which results in a stronger increase of $\mu_{\text{p/n}}$.

The simulations have also shown that the meeting of the fronts does not necessarily imply a p-n junction has formed. Simulations, in which accelerating doping fronts have been observed, show that after meeting of the fronts light emission is initiated, followed after some time by the formation of a p-n junction. This time delay depends on the progress of the doping in the doped regions. If the doping is already maximized before meeting of the fronts, then a p-n junction forms immediately when the fronts meet, e.g. in case $\mu_{\text{ion}}$ is relatively large. Otherwise the p-n junction has to wait until doping maximization has been reached before it can form. The initiation of light emission at the moment that the current is still increasing followed after some time by a significant decrease of the current is in agreement with published data$^{14}$. 

![Figure 15](image.png)
3 Modeling of steady-state behavior in LECs

3.1 Introduction

Light-emitting electrochemical cells (LECs) form an attractive alternative to the organic light-emitting diode (OLED). LECs differ from OLEDs by the presence of mobile ions in the active layer, resulting in a relative insensitivity of the device functionality to active layer thickness and electrode material, which in turn opens the opportunity to fabricate devices comprising solely organic materials by low-cost methods such as printing. However, fifteen years after their invention by Pei et al., the underlying device physics is still far from fully understood. Measurements have been interpreted in either of two models: the electrodynamic model (ED) and the electrochemical doping model (ECD). These models are best distinguished by regarding the predicted steady-state operation of LECs as shown in Figure 16.

![Diagram](image)

**Figure 16 | Schematic diagrams illustrating the potential profile and the electronic and ionic charge distribution in an LEC during steady-state operation.** Potential profiles and charge distributions as predicted by (a) the ED and (b) the ECD. The thick black line represents the potential profile (in eV) and the electronic and ionic charge distribution is illustrated by the red (negatively charged) and green (positively charged) dots. Furthermore, the high and low field regions in the bulk are accentuated by orange and light yellow respectively. In the low field regions, charges are mutually compensated, e.g. cations by anions or cations by electrons.

The former states that all applied potential drops at two sheets of accumulated and uncompensated ions positioned in close proximity to the electrode interfaces (see Figure 16a). Next to the enhancement of carrier injection, these electric double layers (EDLs) screen the bulk polymer from the external electric field, resulting in a diffusion dominated electronic current in the bulk. The ECD predicts EDL formation as well, but only as much of the applied potential is dissipated at the EDLs as is needed to form ohmic contacts (see Figure 16b). The buildup of bulk space charge by the enhanced injection of electronic charge carriers is minimized by the response of the anions and cations. Anions (cations) move away from the electron (hole) injecting contact. Hence, regions are formed in which electrons (holes) are electrostatically compensated by cations (anions). Because of the similarity to the (static) situation encountered in doped inorganic semiconductors, this process is commonly referred to as (electrochemical) doping of the

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* Paragraphs 3.1 – 3.5 and 3.7 have been submitted as ‘A unifying model for the operation of light-emitting electrochemical cells’ by Stephan van Reenen, Piotr Matyba, Andrzej Dzvillevski, René A. J. Janssen, Ludvig Edman and Martijn Kemerink to *J. Am. Chem. Soc.*
conjugated polymer. Since the amount of ions is limited and the amount of injected electrons and holes is not, anions and cations eventually become completely separated\textsuperscript{10}. In between the p- and n-type regions, a narrow intrinsic region arises where the remainder of the applied potential drops and where electron-hole recombination takes place: a light-emitting p-n junction is formed.

Both models are supported by experimental data. Regarding the electrostatic potential, results have been obtained favoring either of the two models\textsuperscript{3,8,30}. Electrochemical doping however, advocated only by the ECD, has been visualized in planar LECs under UV-illumination by monitoring the doping-induced quenching of photoluminescence (PL)\textsuperscript{4,31}. Also modeling studies favoring the ED\textsuperscript{5-8} as well as the ECD\textsuperscript{10,12,13} have appeared. It is clear that the inability of the current models in vogue to explain all experimental and numerical data impedes the further development of LECs.

Here, we present a unified description of LECs. Both the ED and the ECD are shown to be limiting situations of this master model, distinguished by the injection rate at the contacts. The modeling results are confirmed by dedicated experiments and rationalize previous observations. An analytical evaluation of the steady state situation shows that in the doped regions of LECs the drift current cannot exceed the diffusion current, which constrains the maximum device current.

### 3.2 Methods

The numerical model solves the drift-diffusion equations for electrons, holes, anions and cations and Poisson’s equation on an equidistant grid by forward integration in time, see paragraph 1.2 for details. Calculations started from homogenous and equal concentrations of anions and cations (1.25 $\times$ 10$^{25}$ m$^{-3}$ as used by deMello\textsuperscript{7}) and zero electron and hole concentrations, and were allowed to evolve until steady-state had been reached, recognized by a zero ion current. Electron and hole injection past the injection barriers $\Phi_p = \Phi_n = 0.5$ eV was described by different injection models, e.g. Fowler-Nordheim tunneling or Emtage O’Dwyer (see 7.3 for their implementation in the model). For computational ease, a 350 nm thick symmetric device with a bandgap $E_g = 1$ eV and an amount of grid points $N = 81$ was simulated during operation at a bias voltage $V_{bias} = 2$V. It was checked that neither the magnitude of $E_g$ and $V_{bias}$ nor the thickness of the active layer affects the outcome of the calculations in a non-trivial manner, as long as $V_{bias} > E_g$ (See Appendices 7.4 and 7.5). The following additional parameters were used: The relative dielectric constant $\varepsilon = 3$, $T = 300$ K, the electron and hole mobility $\mu_{e/h} = 10^{-6}$ m$^2$V$^{-1}$s$^{-1}$. A relatively high anion and cation mobility could be chosen ($10^{-7}$ m$^2$V$^{-1}$s$^{-1}$) to speed up convergence since this parameter does not affect the outcome at steady-state.

Experiments, comprising scanning Kelvin probe microscopy (SKPM), UV-excited PL, and $I,t$ measurements, were carried out on (non) injection limited LECs. The active layer comprised a conjugated polymer (either MDMO-PPV or SY-PPV, the phenyl-substituted PPV-derivative ‘superyellow’), mixed with the salt KCF$_3$SO$_3$ and the ion-dissolving polymer poly(ethylene oxide) (PEO). The active layer is positioned amid two electrodes, defining an interelectrode gap of approximately 100 $\mu$m. Both types of measurement were performed on nominally identical devices under very similar, controlled
circumstances. To fabricate the non injection limited devices, Au electrodes capped with a layer of Al were deposited by thermal evaporation under high vacuum \((p \approx 1 \times 10^{-6}\) mbar) on top of the spin-coated films. For the injection limited devices, purposely oxidized Al electrodes were utilized instead. The oxidation procedure comprised preparing the spin-coated films in a glove box under \(N_2\) atmosphere in the presence of a small amount of oxygen \(([O_2] \approx 20\text{ ppm})\) before evaporation of Al, and the subsequent storage of the devices for \(~5\) days before testing to allow the formation of an AlO\(_x\) injection barrier.

SKPM images were recorded in a glove box under \(N_2\) atmosphere \(([O_2] < 1\text{ ppm and } [H_2O] < 1\text{ ppm})\) with a Veeco Instruments MultiMode AFM with Nanoscope IV controller, operating in lift mode with a lift height of 25 nm. Ti-Pt coated silicon tips (MikroMasch NSC36/Ti-Pt, \(k \approx 1.75\text{ Nm}^{-1}\)) were employed. All measurements were carried out at \(T = 333\) K.

Optical probing was performed in an optical-access cryostat under high vacuum \((p < 10^{-5}\) mbar\), using a single-lens reflex camera (Canon EOS50) equipped with a macro lens (focal length: 65 mm) and a teleconverter \((\times 2)\). In parallel with the optical probing, the current was measured with a computer-controlled source-measure unit (Keithley 2612). The optical probing was carried out at \(T = 333\) K.

### 3.3 Modeling results

Simulations were done for different injection models (see Appendix 7.3), effectively altering the carrier injection rate. Consequently, one device is injection limited, whereas the other is allowed to form a non-limiting ohmic contact. Figure 17 shows the resulting potential profiles. In the non-limited case, two EDLs have formed near the electrodes, dissipating as much potential as needed to overcome the injection barriers of 0.5 eV. The rest of the potential is dropped over a p-n junction formed in the bulk, in agreement with the ECD. In contrast, when injection is limited, two large EDLs are formed, dissipating nearly all applied potential in accordance with the ED. The electric field profiles shown in the inset clearly indicate that the electric field in the bulk is strongly reduced in the injection limited case as compared to the non-limited device.

**Figure 17**  | **Simulation results for the potential profile in an LEC in steady-state.** The electrostatic potential profile of the device that has (no) injection limitation corresponds to the red (black) line with squares (circles). The corresponding electric field \(E\) is shown in the inset.
The carrier distributions from both simulations are shown in Figure 18. In the non-limited device (Figure 18a) the dopant anions and cations have been spatially separated, either for EDL formation or for doping of the polymer, i.e. for electrostatically compensating injected charge carriers. Due to the symmetry of the simulated device the p-n junction is centered. In the central intrinsic region the charge of the electrons and holes is not compensated due to the absence of dopant ions. Hence, their space charge causes the potential drop observed in this region. This sets organic LECs apart from inorganic p-n junctions in which the space charge results from the ionized dopants.10 The resulting large electric field compensates for the low conductivity in this region, so a constant current density is maintained throughout the device. In contrast, in the injection limited device (Figure 18b) the dopant anions and cations are not fully spatially separated. Still, the ions are used to form EDLs as well as to do some minor doping. However, the doping is much less prominent due to the relatively low concentration of injected charge carriers. Consequently, a large fraction of ions remains paired to their counter ion, instead of to an electron or hole, as in the non-injection limited case. The conductivity is therefore roughly constant throughout the device and no distinct raise of the electric field in the recombination zone is necessary to warrant a constant current density throughout the device. Hence, no p-n junction is formed.

The calculated integrated recombination rate of the modeled LECs (see Figure 18) in steady-state is approximately one decade larger in the ohmic regime than in the injection limited regime. This difference is strongly dependent on the degree of injection limitation and may therefore become even more significant when injection becomes more problematic.

One characteristic that distinguishes LECs from other light-emitting devices like organic and inorganic LEDs with fixed

Figure 18 | Simulation results for carrier and recombination distributions in an LEC. Electron, hole, anion and cation densities are the red, black, green and blue lines, respectively. The orange line represents the recombination profile. No vertical axis is shown corresponding to the latter. The distribution profiles for an LEC in the non-injection limited regime (a) and the injection limited regime are shown (b).
doping is that upon reversing the polarity of the applied potential the device still functions the same: the mobile ions redistribute so that n- and p-doped regions exchange positions\textsuperscript{2,3,4}. The p-n junction is dynamic. This behavior is evidently reproduced in our numerical modeling.

3.4 Experimental results

In order to substantiate the numerical results presented above, experiments were done on planar LECs by scanning Kelvin probe microscopy (SKPM) and electro-optical probing under UV-light.

The results are shown in Figure 19, with the electrode interfaces marked by

Figure 19 | Electrostatic potential profiles in planar LECs during operation and voltage dependence on the interfacial potential drop. a, b, Typical steady-state potential profiles of an LEC during operation at $V = 8V$ in a, the non-injection limited and b, the injection limited regime. The pictures behind the graphs are UV/PL images in steady state, on the same horizontal scale. c, d, Micrographs showing the presence or absence of light emission during steady-state operation at $V = 8V$ in c, the non-injection limited and d, the injection limited regime. The electrode interfaces are indicated by the gray dashed lines in all micrographs. e, The voltage dependent potential drop over the interfacial regions for an injection limited LEC. For positive bias voltages, the green line refers to the positive electrode.
vertical dashed lines. Figure 19a shows the steady-state potential profile of an LEC, with Au/Al top electrodes and SY-PPV as the conjugated polymer, that is not injection limited. The background shows the corresponding optical micrograph. Similar graphs have been obtained for MDMO-PPV-based active layers. In between the two electrodes, two doped regions, where PL is quenched, are visible, sandwiching a narrow junction region where light emission is observed (see Figure 19c). At the electrode interfaces potential drops of ~1.5 and ~1.0 eV are observed, indicating the presence of EDLs. In contrast to previous results on similar devices\(^3\), the potential drop over the EDLs is visible in our SKPM measurements. This is attributed to the use of an Al capping layer on top of the Au layer, which blocks the diffusion of ion-containing material through the electrode\(^3\). Note that equal electrodes are used, so that in order to form ohmic contacts the sum of the potential drops over both EDLs should be approximately equal to the bandgap of SY-PPV, i.e. 2.4 eV\(^32\). This is indeed the case. In the doped regions the potential is more or less constant, whereas a large potential drop is observed in a narrow region in the bulk: the p-n junction. This behavior is fully consistent with the above calculations for a non-injection limited device in the ECD limit (see black line marked by open circles in Figure 17). The final steady-state current through this device during operation was ~1.5 µA. The time dependence of the current will be discussed below.

Injection limitation was achieved by using Al electrodes that were allowed to oxidize slightly. Figure 19b shows the steady-state potential profile of an LEC with Al electrodes that shows all the attributes of being injection limited, as indicated by the large EDLs and the low electric field throughout the entire bulk. Furthermore, no significant doping, as concluded from the absence of PL quenching in the optical micrograph, nor light emission was observed during operation as shown in Figure 19d. The final steady-state current measured through this device was ~0.2 nA, being four orders of magnitude smaller than the current through the device operating in the non-injection limited regime. Hence, the recombination rate will be reduced by a similar factor, beyond the detection limit of the measurement system.

These experimental observations are in very good agreement with the numerical results for an injection limited LEC (see red line marked by solid squares in Figure 17 and Figure 18b). Note, however, that care should be taken not to confuse a non-injection limited device with a p-n junction close to one of the electrodes with an injection limited device, since both may have similar potential profiles. Therefore, the interfacial potential drop of the injection limited LEC was determined as a function of bias voltage, see Figure 19e. The interfacial potential drop increases similarly at both electrodes for biases up to ±8V. More important, at |V\(_{\text{bias}}\)| = 6 V this potential drop surpasses the MDMO-PPV bandgap of ~2.3 eV at both electrode interfaces. A p-n junction that has formed right next to an electrode can result in an interfacial potential drop larger than \(E_g\). However, this cannot occur at both electrodes at the same time, as there can only be a single p-n junction in the device. Since the magnitude of the potential drop at a non-limiting contact in the ECD is at most equal to \(E_g\), the data in Figure 19e allow us to conclude that the device is truly injection limited and behaves according to the ED.
Another major difference between the ED and ECD is that the ED alleges the electronic bulk transport to diffusion rather than drift, since the ions screen the bulk from the external electric field. From the numerical results shown in Figure 17 and Figure 18, the ratio of the drift and diffusion contributions was determined, as shown in Figure 20. For the non-limited case, the drift and diffusion contributions are equal in the doped regions. In the injection limited case, diffusion dominates the total electronic current.

We will now rationalize these observations. First, consider only the ionic current. In steady-state, the total ionic current must be zero, because of the ion-blocking electrodes and the absence of generation and recombination of ions. Thus, in the bulk, the drift and diffusion components of the ion current, $J_{i,\text{drift}}$ and $J_{i,\text{diff}}$ respectively, for both anions ($i = a$) and cations ($i = c$), must be equal but oppositely directed to obtain a zero total current: $J_{i,\text{drift}} = -J_{i,\text{diff}}$. A few steps are required to show that for a device in the ECD limit this implies that $J_{p,\text{drift}} = J_{p,\text{diff}}$ holds for the hole current contributions in the p-doped region, and similar for electrons in the n-doped region. First, charge neutrality applies in the p-doped region, see Figure 18a, so hole and anion densities and their density gradients are equal. Second, holes experience the same electric field as anions. Therefore, the hole and anion drift currents, which are proportional to the product of density and field, are equal in magnitude, apart from a correction factor accounting for the difference in mobility. Also the hole and anion diffusion currents, proportional to the density gradient, are equal in magnitude, again apart from a correction factor accounting for the difference in diffusion constant. According to the Einstein relation the diffusion constant is proportional to the mobility, hence both correction factors are identical and $J_{p,\text{drift}} = J_{p,\text{diff}}$ follows from $J_{i,\text{drift}} = -J_{i,\text{diff}}$. The sign difference is due to the charge difference between holes and anions. A somewhat more elaborate derivation along these lines provides a general relation between the electronic drift and diffusion currents at a position $x$ in the doped region (See Appendix 7.6 for a detailed derivation):

![Figure 20 | Drift-diffusion current ratio profile in simulated LEC devices in steady-state.](image)
\[
\left. \frac{J_{p,\text{drift}}}{J_{p,\text{diff}}} \right|_{x_1} = \tanh \left( \frac{q}{kT} (V(x) - V(x_1)) \right)
\]  \hspace{1cm} (17)

for holes and

\[
\left. \frac{J_{n,\text{drift}}}{J_{n,\text{diff}}} \right|_{x_1} = \tanh \left( -\frac{q}{kT} (V(x) - V(x_1)) \right)
\]  \hspace{1cm} (18)

for electrons, with \( q \) the absolute electronic charge, \( k \) the Boltzmann constant, \( T \) the temperature, \( V \) the electrostatic potential and \( x_1 \) the position of the centre of the recombination zone. Since \( \tanh(y) \) is in between -1 and 1 for any value of \( y \), these relations limit the drift current in steady-state to the diffusion current. The drift-diffusion current ratios in both injection regimes can now be identified. A large value of \( \frac{q}{kT} (V(x) - V(x_1)) \), e.g. due to the presence of a p-n junction – \( \frac{q}{kT} \approx 40 \text{ V}^{-1} \) at 300 K – results in equal drift and diffusion currents. Without a junction, this value becomes smaller, effectively making the diffusion contribution dominant, \( c.f. \) Figure 20.

During the simulations of both devices acting in different injection regimes, also the current vs. time and recombination rate vs. time curves were recorded as shown in Figure 21.

---

**Figure 21** | Transient current density and recombination rate in a simulated LEC device.

Both devices started identically at \( t = 0 \) and were simulated until steady-state was reached. The transient current density (black squares) and recombination rate (orange circles) for an injection limited LEC (a) and an non-injection limited LEC are shown (b). The numbers 1 and 2 mark the initiation of recombination and junction formation respectively. In the insets the calculated current density (black squares) is shown on a linear scale along with the experimental current trace (red). To enable comparison, horizontal and vertical axes have been normalized.

Starting from \( t = 0 \), a large current is observed due to anions and cations moving in opposite directions. The electrodes block the ions, resulting in EDL formation, which reduces the field in the bulk and hence the current goes down. After EDL formation, electrons and holes are injected and move through the active layer until they reach each
other and recombine as denoted in Figure 21 with 1. The LEC in the injection limited ED regime in Figure 21a shows a decreasing current after this point due to further screening of the electric field by increase of the EDLs. In contrast, the LEC in the non injection limited ECD regime in Figure 21b first shows a strong increase in current, which is electronic in nature and is due to doping formation in the bulk. This doping is then maximized, effectively reducing the electric field in the doped regions so that a p-n junction forms, as denoted by 2 in Figure 21b. After junction formation, the ions must adapt to the altered potential profile to reach steady-state. Concomitant with this adaptation, the electronic drift current becomes limited to the diffusion current and thus decreases, as discussed at equations (17) and (18). Because of this, a strong current drop after junction formation is observed in Figure 21b.

Comparison of the results of simulations and experiments in the insets of Figure 21 reveals that the characteristic features of the current transients are well reproduced by the model in both injection regimes. The quantitative differences in current densities and time scales can be attributed to the significantly different device lengths used, i.e. 350 nm in the simulations vs. 100 µm in experiments, in combination with differences in applied bias and mobility values. Nonetheless, the similarity between the results from simulations and experiments convincingly constitutes the physical relevance of the numerical modeling results presented here.

### 3.6 Analytical \( J(V) \)-curve

The results presented in paragraph 3.5 can be used to predict the \( J(V) \) curve of an LEC operating according to the ECD. Note however that the expressions derived in this section all follow from assuming the electron and hole mobility to be independent of doping.

Following equations (17) and (18), the drift and diffusion terms of the electronic current are equal in the doped regions. The combination of conservation of current, drift and diffusion being equal to each other for electrons and holes and a doping independent \( \mu_{p/n} \) results in the anion and cation gradients to be independent of position in the doped regions. Now assume i) the initial, homogeneous concentration of anions, \( \nu_a^0 \) and cations, \( \nu_c^0 \), present in the LEC is known, ii) all cations and anions are separated from each other in steady-state (see Figure 18a) and iii) the amount of uncompensated anions and cations in the EDLs is negligible (see Appendix 7.7). Then the anion and cation distributions have a shape according to Figure 22. Here \( L_p \), \( L_n \) and \( W \) refer to the widths of the p-doped region, n-doped region and the recombination zone respectively. Then in a device with length \( L \), the anion density \( (\nu_a) \) at the electrode interface \( (x = 0) \) can then be easily determined (similar for the cation density at \( x = L) \):
By assuming drift to dominate diffusion in the recombination zone (Figure 20) and the presence of an electric field independent of the position, the recombination zone thickness can be determined:

$$W = \tau_{\text{rec}} \mu_{p/n} \frac{V_{\text{bias}} - E_g}{W},$$

(20)

where $\tau_{\text{rec}}$ is the time in which an electron or hole, after entering the recombination zone, recombines with a hole or electron. After solving equation (20) for $W$ the following expression is obtained:

$$W = \sqrt{\tau_{\text{rec}} \mu (V - E_g)}.$$  

(21)

The thicknesses of the doped regions for a symmetric device is then equal to

$$L_{p/n} = \frac{L - W}{2}.$$  

(22)

The thicknesses of the EDLs are assumed to be insignificant.

The total electronic current density in the p-doped region, $J_{p,\text{total}}$, is equal to twice the diffusion current density:

$$J_{p,\text{total}} = 2J_{p,\text{diff}} = 2qD_p \frac{dn_p}{dx}.$$  

(23)

The hole density gradient is constant and equal to the anion density gradient in the p-doped region. Therefore equations (19),(21) and (22) can be used to express (23) as

$$2qD_p \frac{dn_p}{dx} = 2qD_p \frac{2n_n^0 L}{L_{p/n}} = \frac{16qD_p n_n^0 L}{(L - \sqrt{\tau_{\text{rec}} \mu_{p} (V_{\text{bias}} - E_g)})^2}.$$

$$= \frac{16qD_p n_n^0 L}{(1 - \frac{\sqrt{\tau_{\text{rec}} \mu_{p} (V_{\text{bias}} - E_g)}}{L^2})^2}.$$  

(24)
Since the total current density is equal anywhere in the device in steady-state, this expression for the electronic hole current density in the p-doped region can be used to determine the total current density through the complete device.

Observing the $I(V)$ curve more closely, it is observed that after a sharp increase of the current at $V_{bias} \approx E_g$, the current remains at approximately a constant value for increasing bias. The current is determined by the shape of the ion distribution. An increase in bias leads to an increased recombination zone width. This increase is relatively small for a bias range from 1 to 10V, so that also the current does not increase significantly.

In order to validate the derived analytical expression, a $I(V)$ curve was calculated by the model presented in paragraph 1.2. The following input values were used: $L = 3.5$ $\mu$m, $n_a^0 = n_c^0 = 0.0125$ nm$^{-3}$, $E_g = 1$ eV, $\Phi_p = \Phi_n = 0.5$ eV, $\mu_{p/n} = 1 \cdot 10^{-6}$ m$^2$V$^{-1}$s$^{-1}$, $\epsilon = 3$ and $T = 300$K. The bias voltage was swept from 0 to 100 V. The device was allowed to reach steady-state at each bias value.

The calculated $I(V)$ characteristic is shown in Figure 23. The fit parameters were also analytically determined from the input values and equation (21): $16qD_p n_a^0 L^{-1} = 1.5 \cdot 10^5$ Am$^{-2}$ and $\tau_{rec} \mu_p L^{-2} = 1.3 \cdot 10^{-3}$ V$^{-1}$. The fit parameters following from the best fit of the points in Figure 23 are within the error of these analytically determined values, proving the numerical calculations and the analytical derivation to be in agreement.

One point for improvement of the theory is taking into account the doping dependence of the electron and hole mobility. Interplay is expected between the mobility and the carrier density gradient resulting in a conserved current throughout the device, c.f. equation (23).

Experimentally determined $I(V)$ curves have been reported by e.g. Pei et al.$^2$ and Lei et al.$^{33}$ for devices with an interelectrode distance of 400 and 2000 nm respectively. Their measurements demonstrate a strong increase of the current for increasing bias voltages sufficiently large to inject charges, being a clear qualitative mismatch compared to the analytical $I(V)$ curve. A possible explanation of this difference could be that the LECs had not yet reached steady-state. Both experimental and numerical results shown in Figure 21 demonstrate that this takes relatively long, even after light emission has ceased.
initiated. Another explanation for the mismatch could be the difference between LECs with a thick and thin active layer. Furthermore, the ECD has not yet conclusively been proved for such thin cells, since the recombination zone width in relatively thick cells is of the same size as the thickness of the active layer in thin cells. The scaling of the recombination zone has not been studied thoroughly yet, so an exact scaling of the recombination zone width with the length of the device may not be assumed.

3.7 Conclusion

Two operating regimes in LECs have been identified; their occurrence depends on the ability of the device to form non injection limited ohmic contacts. In the case ohmic contacts are formed, the LEC follows the electrochemical doping model, characterized by the formation of a dynamic p-n junction in the bulk of the device. Anions and cations then become fully spatially separated across the junction, forming electric double layers at the contacts and doped regions in the bulk. In the case injection of electronic charge carriers is limited, doping becomes less pronounced and the ion redistribution increases the electric double layers until the bulk is screened from the external electric field. In this injection-limited regime, the device follows the electrodynamic model and the electronic current is dominated by diffusion. In contrast, in the ohmic regime drift and diffusion contribute equally. Numerical studies as well as experiments confirm these findings.

The equal contribution of drift and diffusion to the total current in the doped regions was used to analytically determine the \( I(V) \) curve of an LEC. In case a doping independent electron and hole mobility was chosen, an \( I(V) \) curve was derived demonstrating a strong increase of the current at \( V_{\text{bias}} \approx E_g \) followed by an approximately constant current for larger bias voltages. Experiments to study the \( I(V) \) curve of LECs have yet to be carried out. Reported experimental data is not in agreement with these findings.

These results imply that the electrochemical doping operation mode, i.e. without contact limitations, is the preferred operational mode for LECs, as it gives the highest current densities and the highest electron-hole recombination rates. They also imply that any degradation in the contact area, either by electrochemical side reactions\(^{34,35}\) or by contact oxidation\(^{36}\) may cause a transition to the electrodynamic operation mode and hence a reduction in current and light output. The often stated independence of LEC operation on contact material should thus be reconsidered\(^ {37}\). Finally, our results show that the operational mode of an LEC-type device may be concluded from the shape of the current transient, and does not per se require elaborate SKPM experiments.
4 Low ion concentration LECs

4.1 Introduction

Light-emitting electrochemical cells differ from other organic devices by the presence of mobile ions in the active layer. These ions are used to dope the organic semiconductor, significantly enhancing carrier injection and conduction. To increase our understanding of the effect these ions have on the properties and processes occurring in LECs, we investigated the transient and steady-state characteristics of LECs with either a relatively large or a relatively low ion concentration. Both experiment and modeling are combined here to facilitate a detailed study of these properties. It is shown that a lowered ion concentration results in a decreased electronic current, leading to a significant change in the ion distribution in steady-state.

Recently Fang et al.\textsuperscript{11} showed the effect of a lowered ion concentration on the doping dynamics in LECs. The lowered ion concentration led to a reduced current through the device and the doping fronts seemed to stop before making contact and forming a p-n junction.

In the following chapters, the consequences of a lowered ion concentration are further studied by the addition of surface potential measurements and numerical modeling of low ion concentration LECs. It is found that in these LECs still doping can form as well as a p-n junction. However, the p-n junction becomes relatively broad and doping less concentrated.

4.2 Methods

The numerical model solves the drift-diffusion equations for electrons, holes, anions and cations and Poisson’s equation on an equidistant grid by forward integration in time (see paragraph 1.2 for details). Calculations started from homogenous and equal concentrations of anions and cations and zero electron and hole concentrations, and were allowed to evolve until steady-state had been reached, recognized by a zero ion current. Several different initial ion concentrations $c_0$ were chosen to study its effect on the steady-state characteristics of LECs: $3.0\cdot10^{-1}$, $5.0\cdot10^{-2}$, $1.0\cdot10^{-2}$, $1.0\cdot10^{-3}$, $1.0\cdot10^{-4}$, $8.0\cdot10^{-5}$ and $1.0\cdot10^{-5}$ ions nm$^{-3}$. Electron and hole injection over injection barriers $\Phi_p = 0.5$ eV and $\Phi_n = 1.5$ eV was described by the ‘modified Boltzmann’ injection model (see Appendix 7.3 for details). An asymmetric device was simulated to make the model more realistic: Au electrodes were used in experiments, resulting in a relatively small $\Phi_p$ and large $\Phi_n$. A 2000 nm thick device with a bandgap $E_g = 2$ eV and an amount of grid points $N = 41$ was simulated during operation at a bias voltage $V_{bias} = 5$V. The following additional parameters were used: The relative dielectric constant $\varepsilon = 3$, $T = 300$ K and an electron and hole mobility $\mu_{p/n} = 5\cdot10^{-11}$ m$^2$V$^{-1}$s$^{-1}$. An anion and cation mobility of $5\cdot10^{-11}$ m$^2$V$^{-1}$s$^{-1}$ was chosen, although this parameter did not affect the outcome at steady-state.

\textsuperscript{*} Part of the experiments presented in this chapter were carried out by Piotr Matyba, Umea University.
Experiments, comprising scanning Kelvin probe microscopy (SKPM), UV-excited PL, and $I,J$ measurements, were carried out on LECs with different PPV/PEO/KTf mass ratios. The mass ratios 1:1.35:0.25 and 1:1.35:0.06 were used to fabricate LECs with a ‘standard’ concentration and a relatively low concentration of ions respectively. The active layer comprised the conjugated polymer SY-PPV mixed with the salt KTf and the ion-dissolving polymer PEO. The active layer is positioned amid two Au electrodes capped with Al, defining an interelectrode gap of approximately 100 µm. SKPM and UV-excited PL was performed on nominally identical devices under very similar, controlled circumstances. All preparation steps were carried out in a glove box under N$_2$ atmosphere ([O$_2$] < 1 ppm and [H$_2$O] < 1 ppm) or in high vacuum.

SKPM images were recorded in a glove box under N$_2$ atmosphere ([O$_2$] < 1 ppm and [H$_2$O] < 1 ppm) with a Veeco Instruments MultiMode AFM with Nanoscope IV controller, operating in lift mode with a lift height of 25 nm. Ti-Pt coated silicon tips (MikroMasch NSC36/Ti-Pt, $k$ ~1.75 Nm$^{-1}$) were employed. All measurements were carried out at $T = 333$ K. Additional measurements at $T = 293$ K were performed on the low ion concentration devices to make the relatively fast processes here-in more discernible.

Optical probing was performed in an optical-access cryostat under high vacuum ($p < 10^{-5}$ mbar), using a single-lens reflex camera (Canon EOS50) equipped with a macro lens (focal length: 65 mm) and a teleconverter ($\times$2). In parallel with the optical probing, the current was measured with a computer-controlled source-measure unit (Keithley 2612). The optical probing was carried out at $T = 333$ K for the ion rich devices and $T = 293$ K for the ion poor devices.

### 4.3 Numerical modeling results

To study the effect of a decreased ion concentration in LECs that function following the electrochemical doping model (ECD), LECs were simulated with different initial

![Figure 24](image-url) | Electrostatic potential and field profiles in modeled LECs during operation in steady-state for different initial ion concentrations.
homogeneous ion concentrations $c_0$. The resultant steady-state electrostatic potential and field distributions are shown in Figure 24.

For each value of $c_0$ except $1.0 \times 10^{-5}$ nm$^{-3}$, a p-n junction arises in between a p- and n-doped region. This is indicated by the relatively large potential drop observed in a limited region. At the interfaces, clear EDLs are observed of which $V_{\text{EDL}}$ is more or less equal to the relevant carrier injection barrier.

Comparison of the electrostatic potential and field profiles reveals three clear trends: for decreasing $c_0$, i) $V_{\text{EDL}}$ decreases, ii) the electric field in the doped regions, $E_{\text{p/n}}$, increases and iii) the undoped junction region broadens, whereas the electric field here, $E_i$, decreases. In case $c_0 = 1.0 \times 10^{-5}$ nm$^{-3}$, no clear p-n junction has formed: the relatively large value of $\Phi_n$ inhibits the injection of electrons due to too few cations being present to overcome this injection barrier. A p-doped region on the opposite side however is formed for $\Phi_p$ is small enough to be overcome.

The three observed trends can be understood by the conservation of current throughout the complete device in steady-state. Since the cations and anions become fully spatially separated from each other (see Appendix 7.6) and the amount of ions used in the EDLs is insignificant (see Appendix 7.7), the effect of a decrease of $c_0$ is the strongest in the doped regions: less doping is possible. Either the doping becomes less concentrated or the doped regions become smaller, effectively increasing the size of the undoped region. In both

![Figure 25](image_url) | Modeled current density (black circles) and recombination rate (orange squares) of LECs with different initial homogeneous ion concentrations $c_0$, biased at 5V. The red line follows the relation $J = A c_0$, for an arbitrary value of $A$, serving as a guide to the eyes.

![Figure 26](image_url) | The difference between anion and cation concentrations in modeled LECs during operation in steady-state for different initial ion concentrations.
cases, the total current through the device decreases (see Figure 25). Note that the recombination rate decreases in a qualitatively similar way. Furthermore, the current decreases nearly linearly. Following the trend of the 4 points corresponding to the lowest ion concentrations, it is observed that the current density of the 5th point is above this trend.

The response of the ions distribution on the decrease of $c_0$ is shown in Figure 26. These profiles represent the absolute difference between the anion and cation density, being proportional to the doping concentration in the device: charge neutrality is approximately valid in the doped regions (c.f. Appendix 7.6) so the ionic charges are compensated by electrons or holes. The doping concentration and the size of the doped regions clearly decrease for decreasing $c_0$. The decrease in doping concentration leads to a lowered electronic current as was already shown in Figure 25. Therefore, to prevent a current density mismatch between the doped and undoped regions, the undoped region becomes broader leading to a decrease in $E_i$. This decrease leads to a reduced drift current and consequently also a total current through this region, since drift dominates this region (c.f. Figure 20). A lowered current also has implications on the injection of charges: less injection is needed, so $V_{EDL}$ decreases as well. Whether the latter is also valid in real devices strongly depends on the density of state of the polymer around the HOMO or LUMO level and disorder effects present in polymers.

All together, an increase of $c_0$ leads to an increase of the potential dropped over the EDLs, an increase of doping and an increase of the field in the junction region by decrease of its width. The observed ‘extra’ increase of the current for an increase of $c_0$ from $1 \times 10^{-2}$ nm$^{-3}$ to $5 \times 10^{-2}$ nm$^{-3}$ (see Figure 25), can be related to a 4th reaction of the device to the increase of $c_0$. In Figure 24, a shift of the junction region is observed towards the contact with the largest injection barrier. The graphs clearly show the larger injection barrier (at $x = 2.0 \, \mu$m) results in relatively much cations (see Figure 26) used for EDL formation and the presence of a relatively large field in the n-doped region compared to the p-doped region. By shifting the junction region, the negative effect of this large injection barrier on the total current is decreased, leading to a relatively strong increase of the current. Then the question remains why this effect occurs mainly at the transition from $c_0 = 1 \times 10^{-2}$ nm$^{-3}$ to $5 \times 10^{-2}$ nm$^{-3}$. This can be explained by the observed less strong increase of doping in the p-doped region at this transition compared to similar transitions at lower ionic concentrations: for increasing $c_0$ from $c_0 = 1 \times 10^{-5}$ nm$^{-3}$ to $1 \times 10^{-2}$ nm$^{-3}$ the doping enhancement occurs more or less linearly in the p-doped region (see Figure 26). At the transition from $1 \times 10^{-2}$ nm$^{-3}$ to $5 \times 10^{-2}$ nm$^{-3}$, this effect is clearly reduced. Furthermore, note the relatively strong decrease of field in the p-doped region during these transitions shown in Figure 24b. Therefore, addition of anions to the device with $c_0 = 1 \times 10^{-2}$ nm$^{-3}$ results in a relatively weak increase of the doping level in the p-doped region and, more pronouncedly, an increase of the width of this doped region, resulting in a shift of the junction region.

4.4 Experimental results

To study the response of LECs to a lowered ion content, two series of devices were prepared with different PPV/PEO/KTf mass ratios: i) 1:1.35:0.25, i.e. ion rich, and ii)
1:1.35:0.06, i.e. ion poor. Characterization of these devices was done by SKPM, UV-excited PL and \( I_t \) measurements during operation at 8V. Both series of devices were tested at an elevated temperature \( T = 333 \text{ K} \). Since the ion poor devices respond relatively fast to the application of 8V at \( T = 333 \text{ K} \), additional measurements were done at \( T = 293 \text{ K} \), effectively slowing down the transient behavior. A typical potential measurement on an ion poor device at \( T = 333 \text{ K} \) is shown in Appendix 7.9. Comparison of the low ion concentration devices at \( T = 293 \text{ K} \) and \( 333 \text{ K} \), reveals that the effect of this lowered ion concentration is similar on the junction region and EDLs, but is not similar on the potential drop over the doped regions. For \( T = 333 \text{ K} \), the potential drop over the doped regions does not increase as clearly, which was however also observed in the calculations (see Figure 24a).

**Figure 27 | Electrostatic potential and field profiles in planar LECs during operation.** a, b, Typical steady-state potential profiles and c, d, electric field distributions of an LEC during operation at \( V_{\text{bias}} = 8V \) with mass ratios PPV:PEO:KTf a, c, 1:1.35:0.25 and b, d, 1:1.35:0.06. The pictures behind the graphs are UV/PL images in steady state, on the same horizontal scale. the electrode interfaces are indicated by the gray dashed lines. d, the black graph corresponds to (b), whereas the red graph is an additional graph of a similar device.
Characteristic results of SKPM and UV-excited PL measurements on both types of LECs in steady-state are shown in Figure 27. Here, steady-state is determined when no more significant development occurs in the potential or doping profile of the device. Note that SKPM and UV-excited PL was performed on similar devices in similar circumstances.

The potential profile of the ion rich device (see Figure 27a) indicates the presence of EDLs. The sum of the here-dissipated potential is approximately equal to $E_g$, i.e. 2.4 eV. Furthermore, doped regions are observed characterized by the presence of a low field in the doped regions (see Figure 27c) and evidenced by the photograph in the background: the dark region corresponds to quenched PL due to doping. In between the doped regions light emission is observed in the photograph coinciding with a p-n junction in the potential profile.

The potential profile of the ion poor device (see Figure 27b) also shows a slightly increased potential drop at the electrodes due to the EDLs. However, here the sum of the interfacial potential drops is much smaller than 2.4 eV. Furthermore, a relatively large $E_{p/n}$ is observed in the doped regions (see Figure 27d), i.e. the dark regions in the photograph (see Figure 27b) in between the two electrodes. The thickness of the p-n junction is relatively large and $E_i$ relatively small. Additionally, the photograph clearly shows the absence of significant doping in this region.

Comparison of these characteristics with the modeling results of an ion rich and ion poor device (c.f. Figure 24 and Figure 26 for $c_0 = 5.0 \cdot 10^{-2}$ and $1.0 \cdot 10^{-4}$ nm$^{-3}$) reveals a striking similarity between experiment and model. Also comparison between ion rich and ion poor devices leads to the same observations for both modeled and real LECs:

![Figure 28 | Photographs and current transients of planar Au/SY-PPV + PEO + KTi/Au LECs with an interelectrode gap of ~90 µm during operation at $V_{bias} = 8V$. Two different PPV:PEO:KTi mass ratios were used: a, b, 1:1.35:0.25 and c, d, 1:1.35:0.06. The modeled current transients are from LECs with an initial homogeneous ion concentration $c_0$ as denoted in the figures. ($I_0$, $t_0$) is b, (5 µA, 150s) for the experiment and (2 kAm$^{-2}$, 0.5 s) for the model and d, (5nA, 1200s) for the experiment and (4 Am$^{-2}$, 0.05s) for the model. The arrows pronounce features that are difficult to distinguish.](image-url)
for decreasing $c_0$, i) $V_{\text{EDL}}$ decreases, ii) $E_{\text{p/n}}$ increases and iii) $E_i$ decreases due to an increase of the thickness of the junction region.

The results of the transient characterization of both types of LECs are shown in Figure 28 and Figure 29a and b. The UV-excited PL measurements on the ion rich device (see Figure 28a) show clear p- and n-type doping front formation. After the doping fronts have met ($t \approx 9s$) light emission is observed in between the p- and n-doped region. The current transient (see Figure 28b) shows an initial drop (indicated by the arrow) of the current after which it rises again ($t = 5s$), corresponding to the increase in doping in the device. The current peak was measured at $t = 30s$. The potential profiles shown in Figure 29a give insight in the transient field distribution in the organic layer. The graphs obtained at $t \approx 10$ and 30s are pointed out as well. From the transient potential profiles, it is observed that the EDLs are almost immediately formed. The black arrows point out the development of the potential distribution in the doped regions. In time, the potential drop over the doped regions decreases so that the potential drop becomes concentrated in an intrinsic region formed in between. In red, the steady-state potential distribution is shown.

**Figure 29** | Transient potential profiles determined by experiments and calculations. The experimentally determined profiles are from LECs with a PPV:PEO:KTf mass ratio of a, 1:1.35:0.25 and b, 1:1.35:0.06. The numerically determined profiles are from LECs with a ion concentration of c, 0.30 ions nm$^{-3}$ and d, 8.0·10$^{-5}$ ions nm$^{-3}$. The red graphs denote the steady-state potential profile and the blue graphs the first profile. The black arrows accentuate the change of the profiles in time and the electrode interfaces are indicated by the gray dashed lines.
At \( t \approx 10\text{s} \) no well-defined p-n junction is measured although light emission is already observed. At \( t \approx 30\text{s} \) a p-n junction becomes more pronounced. Only after \( t > 100\text{s} \), the potential profile has stopped to develop, indicating that the device has finally reached steady-state, although in general in LECs, degradation of the active layer is expected to continue, related to the relatively short life-time of these devices. These potential profiles provide further proof of the conclusions drawn in 3.6 that a current drop occurs when doping is close to maximization and a large potential drop arises in between the doped regions.

Modeling results of the potential profile development in LECs have been added, shown in Figure 29c. Again, the EDLs are almost immediately formed, indicated by relatively large potential drops at \( x = 0 \) and 2 \( \mu \text{m} \). Also the development of the potential in the doped and intrinsic regions is similar as observed in experiments (see Figure 29a). In the calculations, the p-n junction is observed to be off-centre, lying close to the negative electrode. The negative electrode has a larger carrier injection barrier compared to the positive electrode. Therefore, more cations are needed to form an ohmic contact at the negative electrode compared to the amount of anions needed at the positive electrode. The resultant ‘surplus’ of anions in the bulk leads to a larger p-doped region compared to the n-doped region. This follows from the fact that all ions are used for EDL and doping formation and that current is conserved throughout the device. The reason why the junction in the LEC shown in Figure 29a is closer to the positive electrode could be correlated to the larger injection barrier at this electrode as indicated by the relatively large \( V_{\text{EDL}} \) here. However, degradation, side-reactions or asymmetry induced by different carrier mobilities or traps could be related to this observation as well. Therefore, no conclusions can be drawn regarding the position of the experimentally determined p-n junction (Figure 29a).

The UV-excited PL measurements (see Figure 28c) on the ion poor LEC show the presence of p- and n-type doping as well. The doping fronts however stop during progressing towards each other, leaving a relatively large intrinsic region in between. Note the smaller size of the n-doped region compared to the p-doped region. The corresponding current transient is shown in Figure 28d. It is observed that the current drops strongly starting from \( t = 0 \) followed by a small rise (indicated by the arrow). At \( t \approx 600\text{s} \) (c.f. Figure 28c) the current drops again and becomes more or less constant. The development of the potential profile of a similar LEC in similar circumstances was measured with SKPM of which the results are shown in Figure 29b. Initially, a strong potential drop close to the electrodes is observed attributed to EDL formation. Note however that \( V_{\text{EDL}} \) is significantly reduced as compared to the ion rich device (see Figure 29a), as was observed as well in the modeling results shown in Figure 24a. After EDL formation, the bulk potential is observed to redistribute and mainly p-type doping occurs, indicated by the small potential drop over the region just next to the positive electrode. The n-doped region remains relatively small, being in agreement with the photographs of the doping shown in Figure 28c. After \( t \approx 700\text{s} \) (red line in Figure 29b) the development of the potential profile in the ion poor device has more or less ceased.

A current transient of a modeled LEC with \( c_0 = 8 \cdot 10^{-5} \text{ ions nm}^{-3} \) is included in Figure 28b. The corresponding calculated potential profile development is shown in Figure 29d. Again an initial current drop \( (t = 0\text{s}) \) is observed, attributed to the ions redistributing to form EDLs in response to the application of \( V_{\text{bias}} = 5\text{V} \). Then injection is
initiated and doping is formed in the bulk. During these processes, the current is observed to rise slightly. N-type doping is hampered due to the presence of a relatively large electron injection barrier compared to p-type doping. After doping comes close to maximization, a relatively broad p-n junction is formed close to the negative electrode and the current is observed to drop. Again, no conclusions can be drawn on the position of the experimentally determined p-n junction (Figure 29b) due to the absence of side-reactions, degradation etc. in the modeling.

The difference between model and experiment in the ion concentration variation has so far been omitted: in the model, the ion concentration was lowered from $5.0 \cdot 10^{-2}$ to $1.0 \cdot 10^{-4}$ nm$^{-3}$, whereas in the experiment, the amount of added ions was decreased from 0.25 to 0.06. Both the transient and steady-state potential profiles of the model and the experiment shown in Figure 29 are in agreement qualitatively. In addition, the decrease of $I_0$ due to a decrease of $c_0$ is of the order of $10^3$ for both the modeled and measured current transient (see Figure 28). Therefore, the relatively strong decrease of $c_0$ in the model seems justified to describe a decrease of $c_0$ by a factor of 4. In addition, these results indicate that a decrease of ionic content in real, planar LECs has a much stronger effect on the device operation compared to the same adaptation in a modeled LEC. One possible explanation could be a transportation of ions from the active layer in between the electrodes towards regions underneath the electrodes.

Note that also in case of the transient behavior of the LECs, model and experiment seem to be completely in agreement for both the ion rich and ion poor devices, aside from differences in junction positions. The modeled current transients contain the same characteristics as observed experimentally. Also the coupling between features observed in the current transients and characteristics observed in doping and potential profiles are equal for model and experiment as explained above.

### 4.5 Conclusion

The following effects of a decreased ion concentration in LECs have been identified by SKPM and UV-excited PL: a decrease of $V_{EDL}$, an increase of $E_{p/n}$ due to a decreased doping level and an increase of the junction region with a concomitant lowering of $E_i$. Similar effects were observed in modeled LECs while lowering the initial ion concentration. Therefore it is concluded that the observed effects due to a decreased ion concentration can all be related to the decrease in current density through the device. Most strikingly, the model shows a linear increase of the current and light output for increasing ion concentration at a constant bias voltage. An increase of current in real LECs has been observed for increasing ion concentration. More experiments are needed to study the characteristics of this increase.

Additionally, also the transient behavior of ion rich and ion poor LECs was characterized by experiments and numerical modeling. The relevant features of the development of the potential profile and the simultaneously measured current transient obtained from experiments, were convincingly reproduced with the model.
5 Summary and outlook

In today’s struggle for finding more efficient methods for lighting, one breakthrough was the realization of the first light-emitting diode made of organic materials in 1987. Thereafter, this organic LED underwent lots of developments and improvements resulting in the current commercialization of lighting by organic materials. One promising variant of the OLED, first reported in 1995, has however not received much attention: the light-emitting electrochemical cell. This cell is exceptional in organic lighting in that it shows no rectifying behavior and makes use of doping to overcome injection barriers even larger than 1eV by formation of electric double layers. Furthermore, this doping creates the opportunity to fabricate planar cells with large interelectrode gaps, allowing microscopic experimental techniques like scanning Kelvin probe microscopy to study these cells.

Nonetheless, negative device properties such as short life-times and long turn-on times in combination with an ambiguous understanding of its device physics have hindered the interest in LECs by industry and academia. This report attempts to increase this understanding to facilitate the improvement of the mentioned flaws and the development of the LEC by use of experimental, numerical and analytical studies.

These three methods have constructively shown that LECs consisting of a conjugated polymer mixed with an ionic conductor and mobile ions can operate in two dissimilar regimes, separated by a difference in charge carrier injection rate. Hereby, two existing and competing device models have finally been unified: the electrochemical doping model and the electrodynamic model. In case the cell is unable to form ohmic contacts by formation of electric double layers, no significant doping takes place and the majority of the cations and anions remains paired. The injected carriers move through the organic layer driven by diffusion after which they recombine while emitting light. If however ohmic contacts are formed, the cations and anions become fully spatially separated from each other to compensate the large amount of injected charge carriers, forming p- and n-doped regions in the bulk. These regions are separated by a light emitting p-n junction where a significant amount of the applied potential drops. Furthermore, it is shown that the electronic drift and diffusion currents are equal in magnitude and direction in the doped regions in steady-state, exemplifying that the diffusion current may not be neglected in LECs.

To further increase the understanding of the role of the ions, low ion-concentration LECs were studied. The decreased ion concentration resulted in a broadening of the junction region, enhancement of the electric field in the doped regions and a decrease of the potential drop at the electric double layers. These observations were again demonstrated by both numerical calculations and several experimental techniques. The results were interpreted as a reaction to a decreased steady-state current, caused by a decrease in doping due to less ions being available.

Besides the steady-state behavior in LECs, also their transient behavior was considered. The already mentioned long turn-on time of LECs originates from the time needed for the mobile ions to dope the active layer. The manner at which this doping takes place provides interesting device physics. Visualization of this doping in planar cells has revealed the presence of doping fronts moving towards each other until they
collide. Numerical calculations have shown that the formation of these fronts gives insight in the doping dependence of the electron and hole mobility.

One of the main questions that remains after this study is whether LECs with a small interelectrode gap of ~200 nm still operate according to the electrochemical doping model. Techniques like scanning Kelvin probe microscopy and UV-excited PL were used in this report to prove the presence of a dynamic p-n junction in relatively wide, lateral LECs. However, such techniques become inadequate for relatively thin, vertical devices. Recently, Coehoorn et al.\textsuperscript{38} reported the measurement of the emission profile in OLEDs with nanometer spatial resolution by use of an optical outcoupling model. Application of this technique to LECs would be extremely useful to verify whether measurements and modeling done on relatively large interelectrode gap LECs are representative for small interelectrode gap LECs.

Also regarding the doping dynamics in LECs, interesting problems remain. First of all it would be interesting to do a numerical study with a 2D model on LECs, which could give more insight in the fundamentals of the doping dynamics. Gao et al.\textsuperscript{39} for example have shown that when inverting the polarity of the applied bias voltage, the dynamics of the doping fronts significantly change as compared to the dynamics after initial doping of the polymer layer. Furthermore, also a detailed study on the doping front propagation by both experiments and numerical modeling could increase our knowledge about the doping dependence of the electron and hole mobility.

Another interesting observation in the numerical modeling of the transient behavior in LECs is the broadening of the recombination zone starting at the collision of both doping fronts until the p-n junction has finally formed. The modeling shows that this effect is due to the anions and cations passing the recombination zone to become fully spatially separated in order to maximize doping. Recently, Ginger et al.\textsuperscript{37} has reported a broadening of the emission profile during LEC operation, which could originate from the same processes as in the modeling. A detailed study of the recombination zone could give more insight in the processes in this intrinsic region of the LEC. Experimental techniques fit to this purpose are several surface techniques like SKPM or UV-excited PL or measurement of the emission profile as mentioned in the last paragraph.

Finally, the analytically determined $I(V)$ curve has yet to be proved experimentally: published experimental data is not in agreement with the findings reported here. Nonetheless, due to insufficient knowledge regarding the device physics in relatively thin LECs and whether steady-state had been reached or not during these measurements, dedicated experiments are still needed to clear the air regarding this mismatch.
6 References


7 Appendix

7.1 Concerning $V_i$ and $\sigma_i$

For LECs in which doping fronts are studied for different $\mu_{\text{ion}}$ and a doping dependent $\mu_{\text{p/n}}$, the transient potential curves are shown in Figure S1, corresponding to the results shown in Figure 9e-h.

These potential profiles indicate that there is no constant potential drop over the intrinsic region, $V_i$, during doping front propagation. In case of relatively low $\mu_{\text{ion}}$, i.e. $5 \cdot 10^{-12}$ m$^2$V$^{-1}$s$^{-1}$, the potential profile remains more or less constant. This result is due to the ions not being able to react swiftly after injection of mobile charge carriers. Consequently, $V_i$ decreases slowly during propagation.

In case of large values of $\mu_{\text{ion}} = 5 \cdot 10^{-11}$ m$^2$V$^{-1}$s$^{-1}$, the ions react more strongly and a small enhancement of the electric field, i.e. the slope of the potential profile, in the intrinsic area is observed, e.g. compare the potential profiles at $t = 1$ and 5 ms. This field increase drives the front acceleration as was observed in Figure 10 (dark red graph).
For larger values of $\mu_{\text{ion}}$, the electric field is found to be decreasing strongly after injection of charges. This effect can be attributed to the more mobile ions screening the electric field in the bulk of the semiconductor. Hence, the fronts slow down, as was observed in Figure 10 (black and blue graphs).

The development of the ion concentration throughout the modeled LECs is shown in Figure S2.

The position and movement of the doping fronts can be determined by the positions in the bulk where the anion concentration, $a$, and cation concentration, $c$, start to differ strongly. The LEC seems to establish charge neutrality throughout the device except at the EDLs: if no electrons and holes are present, $a \approx c$. After electrons and holes are injected, this expression becomes invalid: $a \neq c$, because the electrons and holes start replacing the anions and the cations respectively to maintain charge neutrality from the EDLs towards the recombination zone which is finally formed.

Furthermore, these results show that the ion concentrations in the intrinsic region remains approximately constant except in the case $\mu_{\text{ion}} = 5 \cdot 10^{-9} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$. Here, $a$ and $c$ clearly decrease around $x = 1000 \text{ nm}$ when the doping fronts get near. Since $a$ and $c$ are
linearly related to the ionic conductivity in the intrinsic area $\sigma_i$; and $\mu_{\text{ion}}$ is a constant, it can be concluded that $\sigma_i$ is not constant during doping front propagation in case $\mu_{\text{ion}}$ is relatively large.

All together it was found that $V_i$ and $\sigma_i$ are not necessarily constants during doping front propagation, which makes the expression found by Robinson et al. inapplicable to describe the front positions versus time graphs shown in paragraph 2.3.2.

### 7.2 Variation of active layer thickness (transient)

The presence of accelerating doping fronts was observed for LECs simulated with different interelectrode gaps. Relevant parameters are: $V_{\text{bias}} = 5\,\text{V}$, $c_0 = 0.3\,\text{nm}^{-3}$, $\mu_{\text{ion}} = 5 \cdot 10^{11}\,\text{m}^2\text{V}^{-1}\text{s}^{-1}$ and a doping dependent $\mu_{p/n}$ were assumed. The results are shown in Figure S3.

Figure S3 | Simulation results of LECs with different interelectrode spacings ranging from 200 to 20000 nm. a-c, The electron (circles) and hole (stars) density profiles during doping front propagation. d, the position of the doping fronts versus time. The inset shows the corresponding absolute values of the front speed where the vertical axis is logarithmic.
Doping fronts are observed for all three length scales. If the sharpness of the doping front is determined by the normalized length scale $\Delta x$ at which the carrier concentration drops by 4 decades, then the sharpness of the doping fronts for small devices is strongly reduced compared to larger devices. However, in case the absolute length scale is used for this purpose, then it is observed that the longer device has a strongly reduced sharpness. This is due to the reduction of the bulk electric field for longer devices, which is the driving force for ions to form doped regions. Due to this reduced electric field, doping takes place relatively slow.

In Figure S3d the propagating doping fronts in all 3 simulated devices are observed to accelerate. Also note that it takes relatively long until the fronts of the device with the largest interelectrode gap finally meet.
7.3 Injection models

In order to obtain different injection rates in the modeled LECs, different injection models have been evaluated in combination with various grid-point spacing. In general, extreme caution should be taken when drawing conclusions from numerical results that depend on the sampling. Here, we deliberately under-sample some of the simulated devices to induce various rates of charge injection. In real devices, as discussed in the main text, injection limitations can be induced by thin oxide layers on the electrodes. Moreover, we will show below that when under-sampling is avoided all injection models yield identical results.

The injection models used in this study were ‘Fowler-Nordheim’\(^40\), ‘Emtage O’Dwyer’\(^41\) and ‘Modified Boltzmann’. The first assumes injection is only mediated by tunneling through a triangular barrier. A more detailed description of this model as used in the numerical modeling can be found in Ref. 42. The injection limited device was simulated by use of this model in combination with 81 grid-points, resulting in a relatively wide tunneling barrier for electrons and holes.

One of the other models, the Emtage O’Dwyer injection model, includes the effect of the image-potential of the injected charge carrier which effectively reduces the injection barrier height \(\Delta\) to \(\Delta'\):\(^43\)

\[
\Delta' = \Delta - q \sqrt{\frac{q E_c}{4 \pi \varepsilon_0 \varepsilon_r}},
\]

where \(q\) is the absolute electronic charge, \(E_c\) is the electric field at the contact plane, \(\varepsilon_0\) is the dielectric constant and \(\varepsilon_r\) is the relative dielectric constant. This injection barrier \(\Delta'\) was subsequently used in a Boltzmann factor to give a boundary condition for the electron \((n)\) or hole \((p)\) density at the electrode as

\[
n(1) = N_0 \exp\left(-\frac{\Delta'}{kT}\right) \tag{S2}
\]

and similarly for \(n(N)\) and \(p(1), p(N)\). Here \(n(i)\) is the electron density at grid point \(i (= 1, \ldots, N)\), \(N_0\) the electron density of states, \(k\) the Boltzmann constant and \(T\) the temperature.

A relatively short grid-point spacing is needed close to the electrodes to avoid under-sampling and to obtain solutions that do not depend on the grid-point spacing with the Fowler-Nordheim and Emtage/O’Dwyer injection models. deMello\(^44\) solved this problem by making use of an adaptive-grid method-of-lines. In order to make simulation of LECs less computationally demanding, another injection model was designed: It uses a Boltzmann factor to describe injection in the following manner taking into account the band bending just behind the first grid-point:

\[
n(1) = N_0 \exp\left(-\frac{\Delta - [V(2) - V(1)]}{kT}\right), \tag{S3}
\]

where \(n(1)\) is the electron density at the first grid-point next to the electrode and \(V(i)\) the potential at grid-point \(i (= 1, 2)\). Hence, the Boltzmann factor is effectively evaluated at
the 2nd grid point. The potential at the first grid point \( V(1) \) is taken as a boundary condition for the potential and is thus constant, \( i.e. \ 0+\Delta \text{ or } V_{\text{bias}}+\Delta \). The potential at the neighboring grid-point however changes due to space-charge accumulated at the EDLs which facilitates injection of electron or holes. In this model injection is not affected by the grid-point spacing and thus thicker devices can be simulated while not having to alter the number of grid-points because of injection problems. The results presented here corresponding to the non-limited or ohmic injection regime were simulated using this injection model.

Simulations have as well been performed proving that all three injection models converge to the same result if a small enough grid-point spacing is chosen, \( i.e. \ L/(N-1)=100/80 \) nm in this case. The results are shown in Figure S4. All relevant properties of the LEC are basically identical for the different injection models in these simulations. By increasing the grid-point spacings for some of the injection models, \( e.g. \) Fowler-Nordheim tunneling injection, the injection rate becomes limited as shown in the main text/paper. However, the results shown here indicate that the precise nature of injection does not influence the device physics. In contrary, only the resultant injection rate has influence on this.
Figure S4 | Simulation results for potential, carrier density and recombination rate distributions in LECs for different injection models. The black, blue and red graphs refer to the Fowler-Nordheim, Modified Boltzmann and Emtage O’Dwyer injection model respectively. a, the potential distribution, b, the ion density distribution, c, the electron and hole density distributions and d, the recombination rate distribution. In b and c, the squares and circles refer to the positive and negative charge carriers respectively.
7.4 Variation of active layer thickness (steady-state)

The simulation results presented in this work are obtained for devices with an active layer thickness $L = 350$ nm, whereas experimental results were obtained for devices with $L = \sim 100$ µm. In order to verify that the conclusions based on the relatively short modeled devices apply to larger devices as well, additional simulations were performed for $L = 3.5$ and 35 µm. The steady-state results for LECs operating in both injection regimes are shown in Figure S5.

The results show that in each injection regime the characteristic features of the potential profiles are similar for each value of $L$. In case of ohmic injection (see Fig. S5a), the potential drop over the EDLs is approximately as large as the injection barriers. The remainder of the potential is dropped over a p-n junction positioned in the centre of the device. The electric field in the junction region is basically independent of the channel length; the different slopes in Figure S5a are due to the normalized $x$-axis. In case of limited injection (see Fig. S5b), only EDLs are observed, dissipating nearly all applied potential to form a field-free bulk.

Concluding, these results show that the characteristics of the presented simulation results are not affected by the length of the active layer, i.e. the inter-electrode gap.

Figure S5 | Simulation results for the potential profile in an LEC in steady-state for different active layer thicknesses $L$. a, The steady-state potential profiles for non injection limited LECs. b, The steady-state potential profiles for injection limited LECs. In the latter, the profiles for $L = 0.35$ and 35 µm are shifted upward and downward by 0.2 eV, respectively for clarity.
7.5 Variation of applied bias

Simulations of LECs with a bandgap $E_g = 1 \text{ eV}$ were carried out for different biases ($V_{\text{bias}}$) up to 10 V. The results during steady-state operation in both injection regimes are shown in Figure S6. The results show that in each injection regime the characteristic features of the potential profiles are similar for each bias applied to the device. In case injection is non-limited (see Fig. S6a), a p-n junction forms for any applied bias voltage exceeding the bandgap. The potential drop over the EDLs is observed to remain constant, whereas the potential drop over the p-n junction increases. In case injection is limited (see Fig. S6b), all potential drops over the EDLs so that the bulk remains more or less field free.

Concluding, these results show that the characteristics of the presented simulation results are not affected by the applied bias, provided it exceeds the bandgap.

Figure S6 | Simulation results for the potential profile in an LEC in steady-state for various applied bias voltages. a, The steady-state potential profiles for non injection limited LECs ($L = 3.5 \mu\text{m}$). b, The steady-state potential profiles for injection limited LECs ($L = 3.5 \mu\text{m}$). In the latter, a horizontal off-set was added to the graphs for clarity.
7.6 Derivation of equations (17) and (18) for electrons and holes

In steady state, charge neutrality in the doped regions is assumed, as has been verified by numerical simulations (see yellow line in Fig. S7) for a device operating in both the ohmic and the injection limited regime.

Figure S7 | The steady-state charge carrier density in a simulated LEC in a) the ohmic regime and b) the injection limited regime. In yellow the absolute value of the difference between the sum of the positive and negative particles is shown. L is 2 µm in a, and 0.35 µm in b.

Generally in steady state, the charge neutrality in the n-doped region is maintained only by electrons, cations and anions:

\[-n + c - a = 0,\]  
(S4)

where \(n, c\) and \(a\) refer to the electron, cation and anion density respectively. In the p-doped region charge neutrality is maintained by holes, anions and cations:

\[p - a + c = 0,\]  
(S5)

where \(p\) refers to the hole density. Taking spatial derivatives, one obtains:

\[\frac{dn}{dx} = -\frac{da}{dx} + \frac{dc}{dx}\]  
(S6)

for the n-doped region and

\[\frac{dp}{dx} = \frac{da}{dx} - \frac{dc}{dx}\]  
(S7)

for the p-doped region.

In steady state, the total ionic current must be equal to zero since ion-blocking contacts are assumed, i.e. they cannot take up or inject ions. From this, it follows that the ion drift current, \(J_{i,\text{diff}}\), must be cancelled by the ion diffusion current, \(J_{i,\text{diff}}\), where \(i = a, c\) for anions and cations, respectively. For anions this can be expressed as follows:
\[
\frac{J_{a,\text{drift}}}{J_{a,\text{diff}}} = -1 = \frac{aq \mu_a}{qD_a} \frac{dV}{dx} = \frac{aq}{kT} \frac{dV}{dx},
\]

(S8)

where \( q \) is the absolute electronic charge, \( \mu_i \) the mobility of charge carrier \( i \), \( D_i \) is the diffusion constant for charge carrier \( i \), \( k \) is Boltzmann’s constant, \( T \) is the temperature and \( V \) is the potential. Here Einstein’s relation will be used to eliminate the diffusion constant.

For holes, the drift divided by the diffusion results in the following expression:

\[
\frac{J_{p,\text{drift}}}{J_{p,\text{diff}}} = \frac{pq \mu_p}{-qD_h} \frac{dV}{dx} = \frac{pq}{kT} \frac{dV}{dx}.
\]

(S9)

By substitution of equations (S5) and (S7) in equation (S9) followed by dividing the result by equation (S8) and taking into account that for any given position, the electric field is the same for ions, electrons and holes, the following result is obtained:

\[
\frac{J_{p,\text{drift}}}{J_{p,\text{diff}}} = \frac{a-c}{a} \frac{da}{dx} = \frac{c-a}{c} \frac{da}{dx}.
\]

(S10)

for holes. For electrons a similar expression is can be found:

\[
\frac{J_{n,\text{drift}}}{J_{n,\text{diff}}} = \frac{c-a}{c} \frac{dc}{dx}.
\]

(S11)

As explained above, the steady-state requirement for anions and cations that drift and diffusion cancel can be expressed as:

\[
J_{a,\text{drift}} = -J_{a,\text{diff}} \quad \text{(S12)}
\]

\[
J_{c,\text{drift}} = -J_{c,\text{diff}} \quad \text{(S13)}
\]

If then the standard drift and diffusion equations are inserted in equations (S12) and (S13) as shown in equation (S8), followed by integration between arbitrarily chosen positions \( x_1 \) and \( x_2 \) and application of separation of variables, the following expressions are obtained:

\[
a(x_2) = a(x_1) \exp \left( \frac{q}{kT} (V(x_2) - V(x_1)) \right)
\]

(S14)

for anions and
\[ c(x_2) = c(x_i) \exp \left( -\frac{q}{kT} (V(x_2) - V(x_1)) \right) \]  
(S15)

for cations. Here \( a(x_i), c(x_i) \) and \( V(x_i) \) refer respectively to the anion density, cation density and the potential at position \( x_i \) \((i = 1, 2)\). These density relations are the well-known Boltzmann expressions which are valid under the condition of a constant electrochemical potential for the ions. In steady state, the ion current is zero and this condition is fulfilled. They imply that in case a p-n junction is present, all ions must become spatially separated to reach steady-state: If \( x_1 \) and \( x_2 \) are respectively taken in the n- and p-doped region on either side of a p-n junction of e.g. 1 V at a device temperature of 300 K, the resultant concentration ratios \( a(x_1)/a(x_2) \) and \( c(x_1)/c(x_2) \) become \( 10^{-16} \) and \( 10^{16} \) respectively.

Now we return to the further derivation of equations (17) and (18) from (S10) and (S11).

In the following, \( \frac{q}{kT} (V(x_2) - V(x_1)) \) is denoted as \( A \) for convenience. Consider the first factor of equation (S10) at any position \( x_2 \) in the p-doped region. Elimination of \( a(x_2) \) and \( c(x_2) \) by substitution of equations (S14) and (S15) where \( x_1 \) can be taken at any position in the bulk of the device, results in the following:

\[
\frac{a_2 - c_2}{a_2} = \frac{a_1 \exp(+A) - c_1 \exp(-A)}{a_1 \exp(+A)}. \tag{S16}
\]

For convenience, the positions of the ion concentrations are denoted with a subscript, e.g. \( a_2 = a(x_2) \). For an LEC in which p- and n-doped regions are present, there should always be a position \( x_1 \) where the anion and cation concentrations are equal, i.e. \( a_1 = c_1 \). In the p-doped region there is a surplus of anions and in the n-doped region there is a surplus of cations. Therefore, both concentrations become equal somewhere in between those regions, i.e. in the recombination zone. Furthermore, equations (S14) and (S15) are still valid in these regions because steady-state is assumed. (S16) can now be further simplified as follows:

\[
\frac{1 - \exp(-2A)}{1} \leq 1. \tag{S17}
\]

For the n-doped region a similar expression is found:

\[
\frac{c_2 - a_2}{c_2} = \frac{1 - \exp(+2A)}{1} \leq 1. \tag{S18}
\]

Now consider the second factor of equation (S10). The following expression can be derived for any position \( x_2 \) in the p-doped region:

\[
\frac{da_2}{dx} - \frac{dc_2}{dx} = \frac{d}{dx} \left( a_2 - c_2 \right) = \frac{d}{dx} \left( a_1 \exp(+A) - c_1 \exp(-A) \right).
\]

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\[
\frac{da_1}{dx} \exp(+A) + a_i \frac{d}{dx} \exp(+A) = \frac{da_i}{dx} \exp(+A) + a_i \frac{d}{dx} \exp(+A) - \frac{dc_1}{dx} \exp(-A) - c_i \frac{d}{dx} \exp(-A)
\]
\[
\frac{da_1}{dx} \exp(+A) - a_i \frac{dA}{dx} \exp(+A)
\]
\[
\frac{da_i}{dx} \exp(+A) - a_i \frac{dA}{dx} \exp(+A) - \frac{dc_i}{dx} \exp(-A) - c_i \frac{dA}{dx} \exp(-A)
\]
\[
\frac{\exp(+A)}{\exp(+A) + \exp(-A)} = \frac{1}{1 + \exp(-2A)} \leq 1
\]

Also here \(x_1\) can be taken at a position where \(a_1 = c_1\). Hence, also the respective drift terms are equal in magnitude. Therefore, to fulfill the necessary steady-state condition that the total ion current is zero, also the anion and cation diffusion terms must be equal at \(x_1\) resulting in: \(\frac{da_1}{dx} = -\frac{dc_1}{dx}\). Substitution in equation (S19) results in

\[
\exp(+A) \left[ \frac{da_i}{dx} - a_i \frac{dA}{dx} \right]
\]
\[
\exp(+A) \left[ \frac{da_1}{dx} - a_i \frac{dA}{dx} - \frac{dc_1}{dx} \exp(-A) - c_i \frac{dA}{dx} \exp(-A) \right]
\]
\[
\exp(+A) \left[ \frac{da_1}{dx} - a_i \frac{dA}{dx} \right]
\]
\[
\exp(+A) + \exp(-A)
\]
\[
\frac{1}{1 + \exp(-2A)} \leq 1
\]

for the p-doped region. For the n-doped region a similar expression is found:

\[
\frac{1}{1 + \exp(+2A)} \leq 1.
\]

By substitution of equations (S17) and (S20) in equation (S10) the following expression is obtained:

\[
\frac{J_{p,\text{drift}}}{J_{p,\text{diff}}} = \frac{1 - \exp(-2A)}{1 + \exp(-2A)} = \tanh \left( \frac{q}{kT} (V(x_2) - V(x_1)) \right)
\]

for the p-doped region and by substitution of equations (S18) and (S21) in equation (S11)
\[ \frac{J_{n,diff}}{J_{n,drift}} = \frac{1 - \exp(2A)}{1 + \exp(2A)} = \tanh\left( -\frac{q}{kT} \left( V(x_2) - V(x_1) \right) \right) \]  

(S23)

is obtained for the n-doped region. Note that \( V(x_1) \) is the potential at the position in between the p- and n-doped regions where \( a(x_1) = c(x_1) \). Therefore, \( V(x_2) - V(x_1) \), is always positive in the p-doped region and negative in the n-doped region. Consequently, \((S22)\) is always positive in the p-doped region, whereas \((s23)\) is always positive in the n-doped region. Equations \((S22)\) and \((S23)\) are equal to equations (17) and (18) in the main text.

### 7.7 Ion concentration in the EDLs

To determine the amount of charge present in an EDL, the EDL and the respective electrode can be regarded as a parallel plate capacitor. From the capacitance, the charge on either plate can then be determined which results in a potential difference \( V_{\text{EDL}} \) between the plates:

\[ \frac{V_{\text{EDL}} \cdot \varepsilon_0 \cdot \varepsilon_r}{d \cdot q} = \sigma, \]

(S24)

where \( d \) is the distance between the plates and \( \sigma \) the surface charge density on the plates. Taking \( V_{\text{EDL}} = 0.5 \) and \( d = 0.3 \) nm, i.e. approximately the distance between two atoms, \( \sigma \) becomes equal to 0.09 nm\(^{-2}\). By assuming the ion sheet to have a finite distance, \( d_{\text{EDL}} \), the charge density \( \rho \) can be approximated by \( \sigma/d_{\text{EDL}} \). If \( d_{\text{EDL}} = 0.3 \) nm as well, then \( \rho = 0.3 \) nm\(^{-3}\). (In simulations where \( L = 350 \) nm and \( N = 81 \): \( \sigma = 0.0064 \) nm\(^{-2}\) and \( \rho = 0.0015 \) nm\(^{-3}\) for \( d = d_{\text{EDL}} = 4.4 \) nm)

In an LEC with a PPV:PEO:KTf mass ratio of 1:1.35:0.25, the ionic volume fraction is 0.25/2.6. The molecular mass of KTf is 188 g/mol = 188\(^{-1}\) mol/cm\(^3\) assuming a density of 1g/cm\(^3\). The density of ions in the active material then equals \( 0.25/(2.6\times188\times6\times10^{23}) = 3.1\times10^{20} \) ions/cm\(^3\) = 3.1\times10\(^{26}\) ions/m\(^3\) = 0.31 ions/nm\(^3\) = \( c_0 \). So in case an extremely thin EDL is chosen approximately one atomic distance away from the electrode in a device of length \( L = 100 \) nm, then only a fraction \( \rho \cdot d_{\text{EDL}} / c_0 \cdot L = 0.003 \) of the ions is consumed in the EDL.

### 7.8 Determination of fit parameters

The calculated \( J(V) \) characteristic shown in Figure 23 was fitted with the following function:

\[ J = \frac{A}{(1 - \sqrt{B(x-1)})^2}, \]

(S25)
where $A = 16qD_p n_n^0 / L$, $B = \frac{\tau_{rec} \mu_p}{L^3}$ and $E_g = 1$ (c.f. equation (24)). To determine fit parameter $A$ for the simulated device, the input values were used as given in paragraph 3.6. Unlike in real devices (c.f. paragraph 7.7), in the modeled LEC a significant part of the ions piles up at the electrodes where their charge is ignored due to the boundary condition of the potential profile at the interfaces (see paragraph 1.2.2). The fraction of ions “lost” at these interfaces in the modeled LEC is plotted against the applied bias voltage as shown in Figure S8 and is equal to $0.5 \pm 0.1$. Consequently, fit parameter $A$ becomes equal to $(1.2 \pm 0.3) \cdot 10^5 \text{Am}^{-2}$.

To determine $\tau_{rec}$ to calculate fit parameter $B$, the FWHM of the peak in the recombination rate profile was plotted against the applied bias voltage as shown in Figure S9 and fitted with equation (21): $\tau_{rec} = (1.7 \pm 0.3) \cdot 10^{-8}$ s. The error was determined by fitting for different values of $\tau_{rec}$ resulting in reasonable fits. The resultant value of $B$ is $(1.4 \pm 0.3) \cdot 10^{-3}$ V$^{-1}$.

![Figure S8](image1.png) | Ion fraction at the electrode interface in a modeled LEC.

![Figure S9](image2.png) | Calculated thickness of the recombination zone in modeled LEC. The red line follows equation (21) with $\mu_p = 1.0 \cdot 10^{-9}$ m$^2$V$^{-1}$s$^{-1}$, $\tau_{rec} = (1.7 \pm 0.3) \cdot 10^{-8}$ s and $E_{gap} = 1$ eV.
7.9 Low ion concentration LEC at 333K

The steady-state surface potential profiles of LECs with Au electrodes capped with Al, measured at \( T = 333 \text{ K} \) and 293 K are shown in Figure S10. Characteristic features observed in a similar device at \( T = 293 \text{K} \) (also shown in Figure 27b) are observed here as well: lowered \( V_{\text{EDL}} \) at both electrodes and a broadened p-n junction.

![Graph showing potential profile in low ion concentration LECs during operation at 8 V at \( T = 293 \text{ K} \) and 333K. The PPV/PEO/KTf mass ratio of this LEC is 1:1:35:0.06. The electrodes are indicated by the gray and pink bars for the black and red graph respectively.]

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