

Engineering Charge Injection Interfaces in Hybrid Light-Emitting Electrochemical Cells

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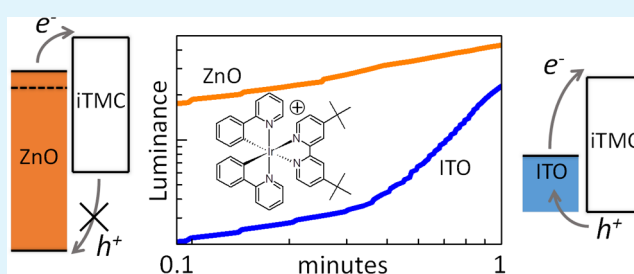
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S Supporting Information

ABSTRACT: Light-emitting electrochemical cells (LECs) consists of a thin film of an ionic organic semiconductor sandwiched between two electrodes. Because of the large density of ions, LECs are often reported to perform independently on the electrodes work function. Here we use metal oxides as charge injection layers and demonstrate that, although electroluminescence is observed independently of the electrodes used, the device performances are strongly dependent on the choice of the interface materials. Relying on metal oxide charge injection layers, such hybrid devices are of interest for real lighting applications and could pave the way for new efficient, stable, low-cost lighting sources.

KEYWORDS: LECs, iridium complex, OLEDs, electroluminescence, organic electronics, metal oxides



The stage of development of organic light-emitting diodes (OLEDs) is so advanced that these devices are now competing with established technologies in the display market. On the other side, the successful introduction of OLEDs into the lighting market will depend essentially on a reduction of the associated production costs. For this reason, novel materials as well as different device architectures are continuously being investigated. Light-emitting electrochemical cells (LECs) are much simpler types of electroluminescent devices, relying on a single ionic solution processed light-emitting layer sandwiched in between two electrodes.¹ Two types of emitters have been explored so far, (i) conjugated polymers blended with salt or ionic liquids² and (ii) ionic transition metal complexes (iTMCs).³ The latter have been the subject of intense research due to the intrinsic higher photoluminescence quantum yield (PLQY) associated with phosphorescent emitters, resulting in higher power conversion efficiency (PCE).^{4,5} The key features of LECs is the high concentration of ionic species in the emitting layer, which redistribute after application of an external bias forming interfacial electric double layers (EDLs).^{6,7} EDLs generate strong fields able to assist the injection of holes and electrons at the anode and cathode, respectively. For this reason, LECs are often reported to perform independently on the work function of the electrodes used.⁸ This statement is only partially true, as we will demonstrate later in our discussion. As higher voltages are applied, increasing charges are injected into the active material leading to its oxidation

and reduction, in a similar fashion to what is obtained by chemical p- and n-doping in state of the art OLEDs.^{9,10} Hence, the applied potential drops in-between the doped zones over the low-conductive intrinsic region, where the light emission occurs.¹¹ Within this perspective, the maximum PCE would be obtained when the carrier recombination zone (intrinsic region) is located near the center of the active layer, where exciton quenching at the electrodes is minimized. Assuming a balanced ambipolar mobility of the semiconductor, the position of the recombination zone will depend mainly on the equilibrium between the processes of hole and electron injection.¹¹ In this letter, we correlate the brightness, efficiency and turn-on time (t_{on}) of efficient and stable LECs with the work function and the properties of the charge injection materials used. Despite of the wide range of commercially available charge injecting, transporting, and blocking molecular materials,¹² we focused on architectures employing metal oxides thin films. Metal oxides charge injection layers have been chosen because of their unique properties of high carrier mobility, high transparency and the intrinsic stability toward moisture and oxygen.^{13,14} Thanks to these unique features, metal oxides have been widely employed in a variety of efficient organic optoelectronic devices.^{15–18} In particular, we used zinc

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oxide (ZnO) and molybdenum trioxide (MoO_3) as the electron and hole injection layers (EIL and HIL), respectively. ZnO is a n-type semiconductor with a conduction band edge (E_c) close in energy to the lowest unoccupied molecular orbital (LUMO) of the iTMC used in this work (Figure 1).¹⁹ On the other side,

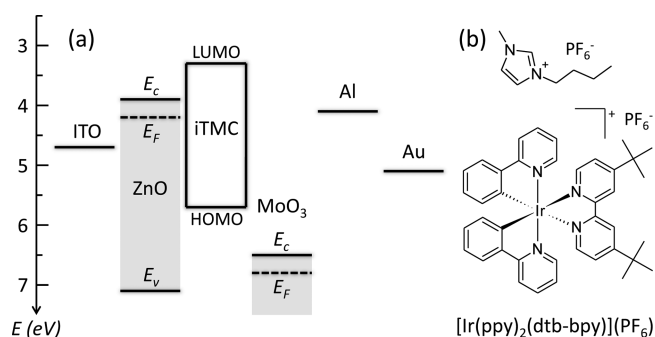


Figure 1. (a) Energy-levels for the materials employed in this work and (b) chemical structure of the ionic liquid and the iTMC constituting the light-emitting layer. Energy levels for the inorganic materials are taken from literature, while the iTMC bands have been determined experimentally from photoelectron spectroscopy in air (PESA) and UV-vis absorption spectra (see the Supporting Information).

the Fermi level (E_F) of MoO_3 is so large that the use of thin films of MoO_3 as hole injection layers leads to ohmic contacts with most organic semiconductors.^{20,21} We demonstrate that although electroluminescence generation in LECs is rather independent from the type of charge injection material or electrode used, their work function and exciton blocking property strongly influence the device performances.

The iTMC used as the light-emitting material is the $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})](\text{PF}_6)$ (Figure 1b), where ppy is 2-phenylpyridinato and dtbbpy is 4,4'-di(*tert*-butyl)-2,2'-bipyridine, synthesized according to previously described methods.²² LECs were prepared on prepatterned indium tin oxide (ITO)-coated glass plates, which were thoroughly cleaned by subsequent sonication in aqueous detergent, water, and 2-propanol baths, and activated by exposure to a UV-ozone lamp. ZnO thin films were prepared by spin coating a solution of zinc acetate dihydrate (10 mg mL^{-1} in ethanol:water:acetic acid, volume ratio 50:2:1) on the ITO-coated substrates, and by annealing them on a hot plate at $450 \text{ }^\circ\text{C}$ for 2 h. Thin films (100 nm) of the iTMC were obtained by spin-coating a solution in acetonitrile. To improve the ionic conductivity of the layer,²³ we added the ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{BMIM}](\text{PF}_6)$, Figure 1b) to the iTMC solution, resulting in a molar ratio iTMC:IL of 4:1. Metals (Al, Au) and MoO_3 thin films were deposited through a shadow mask with a thermal vacuum-evaporation system integrated in an inert atmosphere glovebox. The active area of the devices was 6.5 mm^2 . The LECs were not encapsulated and characterized inside the glovebox by applying pulsed current ($J = 200 \text{ A m}^{-2}$, 1 kHz, 50% duty cycle) and monitoring the voltage and luminance with a True Color Sensor MAZeT (MTCSiCT Sensor) using a Botest OLT OLED Lifetime-Test System.

We first describe the properties of hole injection into the iTMC layer by using bare and MoO_3 coated ITO as the anode and Al or Au as the cathode. Devices were driven with pulsed current with a maximum current density $J_{\text{max}} = 200 \text{ A m}^{-2}$ and a

duty cycle of 50%, resulting in an average current density $J_{\text{avg}} = 100 \text{ A m}^{-2}$. Performances over time as well as the key parameters for this set of devices are reported in Figure 2 and

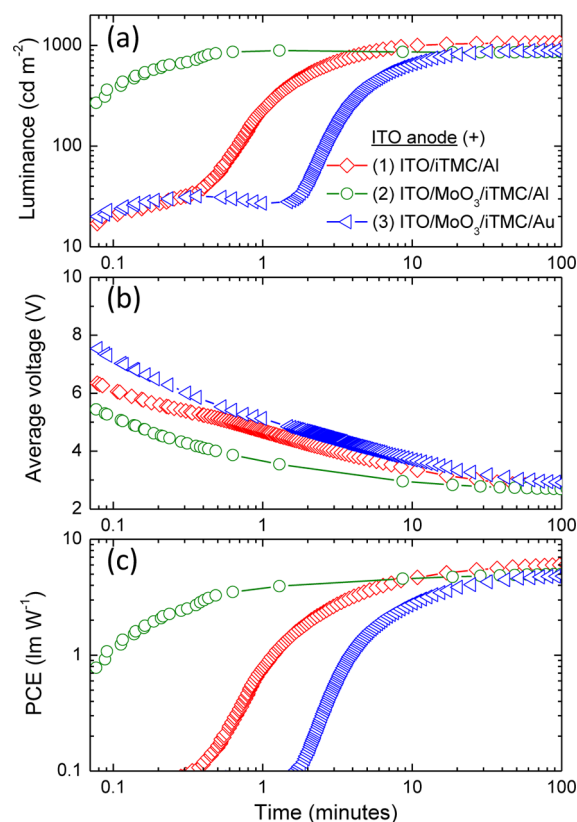


Figure 2. (a) Luminance, (b) average measured voltage, and (c) PCE characteristics versus time for a series of devices where the ITO is used as the anode (positively biased).

Table 1. Key Performance Parameters for a Series of LECs Where ITO Is Used As the Anode^a

	L_0 (cd m^{-2})	t_{on} (s)	L_{max} (cd m^{-2})	t_{max} (min)	PCE_{max} (lm W^{-1})	EQE_{max} (%)
(1) ITO/ iTMC/Al	17	41	1059	100	6.0	3.5
(2) ITO/ MoO_3 / iTMC/Al	269		888	1	5.0	2.9
(3) ITO/ MoO_3 / iTMC/Au	20	158	893	100	4.8	2.9

^a L_0 , luminance at time $t = 0$; t_{on} , turn-on time; L_{max} , maximum luminance; t_{max} , time to maximum luminance; PCE_{max} , maximum power conversion efficiency; EQE_{max} , maximum external quantum efficiency.

Table 1, respectively. The device with bare ITO anode and structure ITO/iTMC/Al (1) shows a slow rise of the electroluminescence with a turn-on time t_{on} (here defined as the time needed to reach a luminance of 100 cd m^{-2}) of 41 s. Luminance steadily increased until reaching a maximum $L_{\text{max}} = 1059 \text{ cd m}^{-2}$ at 100 min, corresponding to a maximum $\text{PCE}_{\text{max}} = 6 \text{ lm W}^{-1}$. This behavior indicates an injection limited regime dominated by the dynamics of ions accumulations at the

interfaces (formation of EDLs).^{24,25} In this regime, the current flowing through the device recombines at/close to one interface and is dissipated through direct charge recombination and exciton quenching. Once EDLs build up, p- and n-doping of the iTMC take place, moving the recombination zone toward the center of the active layer with a substantial increase of photon generation. Insertion of a thin (10 nm) film of MoO₃ in between the ITO anode and the iTMC (device 2) results in a substantial change of the device performances. First of all, electroluminescence is instantaneous and intense with an initial luminance $L_0 = 269 \text{ cd m}^{-2}$, meaning that the barrier for hole injection no longer exists upon coating of the ITO with MoO₃. This hypothesis is also supported by a reduction of about 2 V in the average voltage measured at time $t = 0$ (t_0) after inserting the MoO₃. Both luminance and PCE increase fast at the beginning of measurements (note the log scale of the time domain), reaching $L_{\text{max}} = 888 \text{ cd m}^{-2}$ and $\text{PCE}_{\text{max}} = 5 \text{ lm W}^{-1}$ only 1 min after biasing the device. These values are somewhat lower compared to what obtained for device (1), most likely due to the proximity of the exciton recombination zone to the Al cathode, consequence of the ohmic hole injection. As an extreme case we also fabricated a device with MoO₃ HIL but using a Au cathode instead. As expected, this LEC (device 3) shows a large t_{on} of 158 s, consequence of the wide electron injection barrier, and the maximum luminance and efficiency are only achieved after about 100 min of device operations. Interestingly, the device still reaches high luminance and PCE ($L_{\text{max}} = 893 \text{ cd m}^{-2}$ and $\text{PCE}_{\text{max}} = 4.8 \text{ lm W}^{-1}$), indicating that LECs can indeed efficiently generate electroluminescence independently of the electrodes work function, but at the cost of viable switching speeds.

A common feature of the first set of LECs is the presence of a rather high electron injection barrier at the iTMC/Al interface (Figure 1a), evident also from the measured average voltage V_{avg} reported in Figure 2b. All LECs show a relatively high voltage at the beginning of the measurements which, due to the generation of doped zones, steadily decreases for converging to the value $V_{\text{avg}} = 2.7 \text{ V}$, corresponding to the band gap of the iTMC ($\sim 2.7 \text{ eV}$). This is true also in the case of the device with the ohmic ITO/MoO₃/iTMC contact, which shows an initial $V_{\text{avg}} = 5.4 \text{ V}$, confirming the presence of the electron injection barrier. The use of low work function metal electrodes such as Ba or Ca has been shown to lead to ohmic electron injection into iTMC,¹² but their high reactivity toward oxygen and moisture would require a rigorous encapsulation of the device, undermining the intrinsic simplicity of LECs. Hence, the electron injection interface was modified by the insertion of solution processed ZnO thin films. For this purpose, we adopted the inverted configuration where the ITO is used as the cathode,²⁶ since ZnO cannot be processed from solution on top of the iTMC layer. Performances over time as well as the key parameters for this series of inverted devices are reported in Figure 3 and Table 2, respectively. A LEC with bare ITO cathode and Au anode is used as the reference (device 4). As expected from the energy difference between the ITO work function and the iTMC LUMO (1.6 eV), the device is strongly injection limited with an initial V_{avg} as large as 9 V and poor luminance $L_0 = 4 \text{ cd m}^{-2}$. As the EDLs form and the doped regions start growing, electroluminescence slowly rises with a $t_{\text{on}} = 48 \text{ s}$, stabilizing around $L_{\text{max}} = 300 \text{ cd m}^{-2}$ after 2.5 min driving. The PCE, however, remains quite low due to the unbalanced charge injection causing the recombination zone to be close to the ITO cathode. The insertion of a ZnO EIL

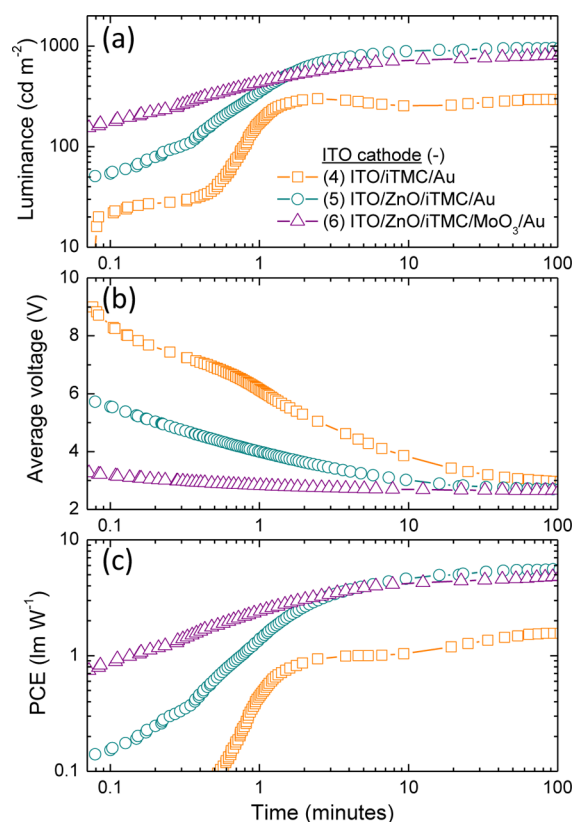


Figure 3. (a) Luminance, (b) average measured voltage, and (c) PCE characteristics versus time for a series of devices where the ITO is used as the cathode (negatively biased).

Table 2. Key Performance Parameters for a Series of LECs Where ITO Is Used As the Cathode^a

	L_0 (cd m^{-2})	t_{on} (s)	L_{max} (cd m^{-2})	t_{max} (min)	PCE_{max} (lm W^{-1})	EQE_{max} (%)
(4) ITO/ iTMC/Au	4	48	300	2.46	1.6	1.0
(5) ITO/ZnO/ iTMC/Au	51	18	955	93	5.5	3.1
(6) ITO/ZnO/ iTMC/ MoO ₃ /Au	154	-	820	92	4.8	2.7

^a L_0 , luminance at time $t = 0$; t_{on} , turn-on time; L_{max} , maximum luminance; t_{max} , time to maximum luminance; PCE_{max} , maximum power conversion efficiency; EQE_{max} , maximum external quantum efficiency.

(device 5) strongly improves the device characteristics. Immediately after biasing the LEC, the measured electroluminescence is $L_0 = 51 \text{ cd m}^{-2}$ and V_{avg} is reduced to 5.7 V. The luminance increases fast ($t_{\text{on}} = 18 \text{ s}$) reaching 800 cd m^{-2} after 2 min and $L_{\text{max}} = 955 \text{ cd m}^{-2}$. The PCE is comparable to what measured for the first series of devices (Figure 2), with $\text{PCE}_{\text{max}} = 5.5 \text{ lm W}^{-1}$. As opposite to metal electrodes, the role of ZnO is 2-fold, enhancing the electron injection into the iTMC LUMO while, at the same time, confining the injected holes into the active layer. Despite of the favorable performances, device 5 still suffers from a limited injection since the measured voltage takes about 10 min to converge to the value of the band gap of the iTMC. A balanced charge injection can be achieved through the contemporary use of a ZnO EIL and a MoO₃ HIL (device 6). This device architecture leads to a large

improvement in the device performances, with instantaneous and intense electroluminescence ($L_0 = 154 \text{ cd m}^{-2}$) and an initial measured voltage as low as 3.3 V, indicating a very efficient charge injection into the iTMC, even without the assistance of EDLs at the interfaces.

On the other hand, PCE_{max} is limited to 4.8 lm W^{-1} , suggesting that nonradiative recombination processes take place. Since the process of hole injection can be considered ohmic, the exciton recombination zone is likely to extend close to the ZnO/iTMC interface, where a small electron injection barrier still exists. While the energetics of this interface allows to exclude the direct hole recombination at the cathode, excitons formed in its proximity could be separated via charge transfer with a mechanism analogous to that of dye-sensitized solar cells. Moreover, interfacial dipoles pinning the Fermi levels at the organic/inorganic interfaces are not taken into account in the discussions, and they might have an additional and significant influence on the charge injection dynamics in hybrid LECs. The use of metal oxides, however, remains very advantageous due to their ability to confine carriers in the active layer and to reduce the exciton quenching observed at metallic interfaces. Last but not least, these materials are intrinsically more stable compared to low work function electrodes or traditional organic electronics materials, and their application is of special interest for simple low-cost optoelectronics devices.

In conclusion, we have demonstrated efficient hybrid LECs employing metal oxides as charge injecting materials. Although electroluminescence from the iTMC is observed independently of the electrodes used, their performances are strongly dependent on the choice of the materials at the interfaces. Maximum device efficiency and luminance, for example, are mainly determined from the equilibrium between the processes of hole and electron injection. As a matter of fact, even in injection limited devices, the formation of EDLs at the interfaces and the subsequent propagation of highly conductive doped regions can lead to bright and efficient electroluminescence. On the other side, fast device switching requires the minimization of the barrier for hole and electron injection, which can be easily achieved by using charge selective contact such as ZnO and MoO_3 , respectively. Such hybrid device architecture is of particular interest for real lighting applications, because it meets at the same time the requirement of speed, brightness and efficiency. Moreover, relying on metal oxide charge injection layers, hybrid LECs could pave the way for new environmentally stable, low-cost lighting sources.

■ ASSOCIATED CONTENT

Supporting Information

UV-vis absorption spectrum and PESA spectrum for the iTMC. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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