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# Charge injection barrier modification in organic LEDs

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Balanced injection of positive and negative charge carriers is a key issue for the operation of highly efficient organic light emitting devices at low operating voltage. In this article, we will give an overview of our investigations on the optimization of charge carrier injection from the anode and the cathode into organic semiconductors. These investigations include proper pretreatment of the indium–tin oxide substrate, and stacking of several organic hole transporting layers to increase the hole injection current from the transparent anode into the emissive layer. On the cathode side, binary metal alloys, and the effect of an insulating layer between the respective metal cathode and the first electron transporting layer are investigated.

## Introduction

In organic light emitting devices (OLEDs), photons are generated by a binary recombination process of holes and electrons in the emissive layer. In other words, a balanced injection of positive and negative charge carriers into the emissive organic layer is crucial for achieving high quantum efficiency.[1]

On the anode side, it can be shown, that an appropriate choice of the hole transporting material adjacent to the ITO will result in an ohmic contact.[2] Thus, the current of positive charge carriers is not dominated by the injection properties of the anode, but by space charge effects within the organic hole transport layers. Even so, proper ITO pretreatment by means of reactive ion etching (RIE) and/or UV–ozone cleaning has a positive impact on long term device stability.[3–5] Further, by combining several hole transporting layers with appropriate energy levels of the highest occupied molecular orbitals (HOMOs), internal energy barriers can be reduced, and the positive charge carrier concentration in the emissive region can be increased dramatically.[6]

On the other side, the electron injection current from the cathode can be improved by proper choice of the cathode metal[7] or by usage of binary alloys.[8] Thin insulating layers (*e.g.* LiF) between the cathode and the first electron transporting layer allow the usage of air-stable cathode metals like *e.g.* aluminum instead of moisture- and oxygen-sensitive metals like, *e.g.* magnesium or calcium. Additionally, they improve device efficiency and lifetime.[9]

In our experiments, OLEDs comprising small functional molecules as well as polymer devices based on fluorene-type polymers were investigated with respect to charge injection optimization.

## Optimization of the transparent anode

Due to its high transparency and low sheet resistance, indium–tin oxide (ITO) is the standard anode material in OLED technology. In our experiments, we used ITO-coated glass substrates with a sheet resistance of less than 20 Ω/❑. The ITO layer was patterned by a conventional photolithographic process. Before coating with the organic material, all substrates were cleaned using acetone and methanol.

In Fig. 1, measurements on a "single carrier" device are depicted. An ITO substrate is coated with a layer of 300 nm thickness of a starburst-shaped amine derivative, namely 4,4′,4″-tris{*N*-(3-methylphenyl)-*N*-phenylamino}triphenylamine (*m*-MTDATA). As counter electrode, a silver layer is used. A voltage step of about 4 V is applied and the current signal is observed. After the initial current peak which is due to the charge-up of the diode capacitor, a strong peak in current density can be observed which indicates a space charge limited current density. This is clear evidence for an ohmic contact between ITO and *m*-MTDATA, as it was also reported by Giebeler *et al.*[2] Thus, an appropriate choice of the hole transporting layer adjacent to the ITO will render the current of positive charge carriers limited by space charge effects instead of injection.

Even so, an ohmic contact for hole injection is not sufficient for achieving optimum charge carrier concentration in the active organic layer. Device efficiency and long term stability can significantly be increased by proper pretreatment of the

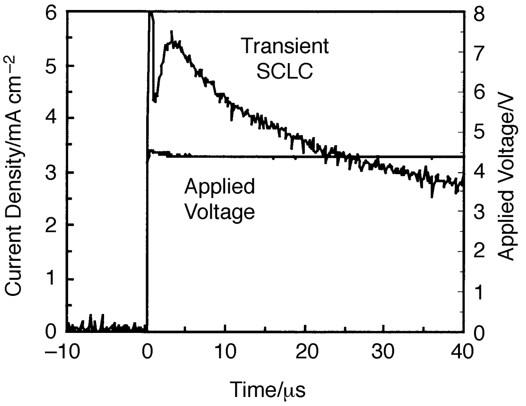

**Fig. 1** Transient space charge limited current (SCLC) in ITO/300 nm *m*-MTDATA/Ag with ITO biased positively. *Ca.* 5 µs after applying a voltage step, a maximum in current density appears. This is clear evidence for an ohmic contact of *m*-MTDATA on ITO.[2]

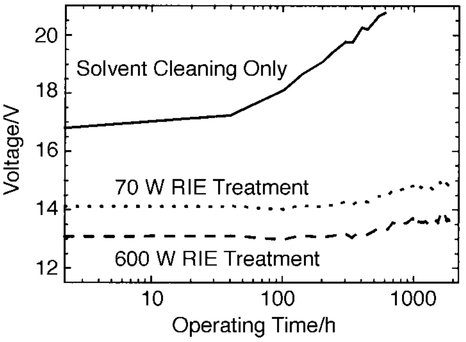

**Fig. 2** Impact of ITO pretreatment by solvent cleaning and reactive ion etching (RIE) on the operating voltage of devices based on functional molecules. Devices are driven by a pulsed current excitation with a duty cycle of 1 : 16.

ITO surface. In Fig. 2, the operating voltage of devices consisting of copper phthalocyanine (20 nm), *N*,*N*′-di(naphthalen-1-yl)-*N*,*N*′-diphenylbenzidine (α-NPD, 100 nm) and tris(8-hydroxyquinolino)aluminum ($Alq_3$, 50 nm) and a Mg : Ag 10 : 1 cathode (150 nm) are depicted as a function of operating time. The devices are driven in a pulsed mode with a duty cycle of 1 : 16. In these experiments, the ITO surface was pretreated by different procedures. The first substrate was purified only by ultrasonic cleaning in acetone and methanol. The other substrates were pretreated additionally by reactive oxygen ion etching (RIE) in a plasma reactor (Materials Research Corp., Model MIE 720). Exposure time was 90 s with plasma powers of 70 and 600 W, respectively. Devices treated by solvent cleaning only exhibit a high starting level and a significant rise in operating voltage with operating time. On the contrary, devices on substrates pretreated by RIE start at a lower voltage level and exhibit nearly no rise in operating voltage. We attribute this effect to a removal of contaminating residues at the ITO surface on one hand and a shift in work function of the ITO on the other. This shift might be due to a change in stoichiometry of the indium–tin oxide.[10,11]

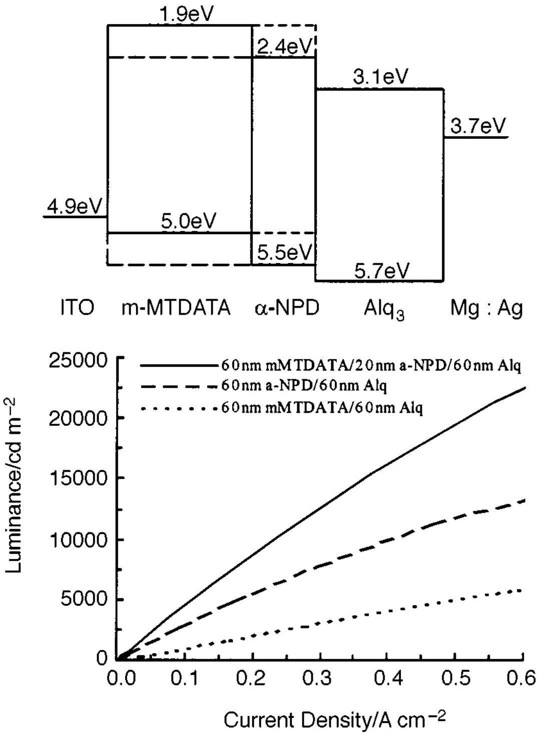

**Fig. 3** Upper part: formation of a "hole-staircase" on an energetic scale by combination of appropriate hole transporting layers (energy levels according to ref. 12–14). Lower part: increase of device efficiency.

However, at very harsh plasma conditions, the positive effect of the etching is more than balanced by thermally induced damage of the ITO surface. Thus, in our experimental setup, there is a broad optimum RIE power at *ca.* 500–600 W.

With an optimized ITO surface and a hole transporting layer adjacent to the anode which form an ohmic contact, still further effort is necessary to improve the density of positive charge carriers in the emissive layer. This is mostly due to the large energy barrier which holes have to overcome to get into the highest occupied molecular orbital (HOMO) of the $Alq_3$, the layer in which recombination takes place. Thus, a multilayer structure of several hole transporting materials with HOMOs forming a "staircase" is advantageous.

In Fig. 3, the impact of the above mentioned hole staircase on device efficiency is depicted. *m*-MTDATA forms an ohmic contact with ITO, but due to the large energy barrier between the HOMOs of $Alq_3$ and *m*-MTDATA, the efficiency of this double-layer structure is the lowest in comparison to multilayer setups. In α-NPD-$Alq_3$ devices, on the other hand, a large energetic barrier at the ITO-hole transporting layer interface prevents high quantum efficiencies. The advantage of multilayer structures is obvious. With respect to display fabrication cost, an optimum has to be found between high-performance high-cost multilayer structures on one hand and lower-performance lower-cost setups with a reduced number of layers on the other hand.

## Optimization of electron injection

Electron injection into organic light emitting diodes is provided by top metal cathode layers. In devices consisting of functional molecules, $Alq_3$ is a very efficient standard electron transporting and emitter material. In polymer devices, our experiments are focussed on fluorene-based electron transporting materials (FETP, provided by DOW Chemical Corp., Midland, USA).

In order to improve the electron injection current into the emissive region, a proper choice of the cathode material is essential. To reduce the energetic barrier between the electrode and the electron transporting material, the work function of the metallic cathode has to be very low. On the other hand, low work function materials are very reactive under ambient conditions and, thus, reduce device stability and lifetime. For metals with work functions considerably lower than 3.0 eV, the advantage of enhanced electron injection can be more than offset by the disadvantage of oxidation during metal deposition, dark spot formation during operation and reactions with the adjacent organic material.

One promising solution of this problem is the usage of cathodes consisting of alloys of an efficiently electron-injecting low work function metal like Mg, Ca *etc.* and an air-stable noble metal like Ag.[8]

On Fig. 4 (upper part), device efficiencies are given for polymer devices with calcium–silver cathodes as a function of silver content. No significant drop in device efficiency can be observed up to a silver concentration of about 30%. There even appears to be a slight efficiency maximum at about 20% silver. During operation (Fig. 4, lower part) in inert gas atmosphere under display driving conditions described above, devices with Ca : Ag 80 : 20-cathodes exhibit a reduced initial drop and a prolonged lifetime. Thus, appropriate coevaporated or even cosputtered cathode alloys are advantageous for organic light emitting devices for display applications or illumination purposes.

In contrast to this progress, cathodes comprising reactive low work function metals still exhibit disadvantages with respect to device operating stability. Thus, the search for new electron injection concepts still is a challenge. For example, the application of metal insulator semiconductor (MIS) structures to organic light emitting devices seems to be a promising

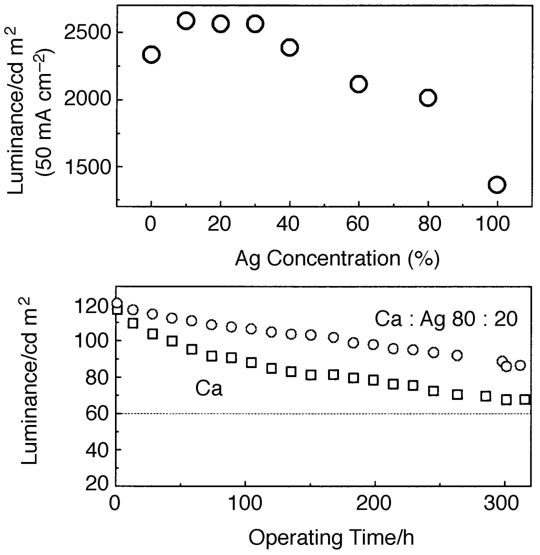

**Fig. 4** Upper part: device efficiency of fluorene-based polymer devices with co-evaporated Ca : Ag cathodes as a function of Ag concentration. Lower Part: lifetime of polymer devices with Ca : Ag cathodes in comparison with pure Ca cathodes.

approach. In these structures, air-stable cathode metals with high work functions are used. To avoid the disadvantage of low device efficiency resulting from the energetic mismatch of the Fermi level and the lowest unoccupied molecular orbital (LUMO) of the adjacent electron transporting material, thin insulating films are inserted between metal and organic material. Due to the large voltage drop in the insulating layer during device operation and band bending effects[9] the Fermi level of the metal and the LUMO of the electron transport material are nearly aligned again. Then, electron injection might occur by tunneling through the thin insulating film. Besides, electron injection can be enhanced by formation of thin dipole layers or chemical reactions of the intermediate layer material with the adjacent organic layer.

Under appropriate conditions, device efficiency of OLEDs with thin insulating layers are even much higher than the corresponding values of devices with low work function metal electrodes.

Efficiency and onset voltage of OLEDs with insulating layer cathodes on polymer and on functional molecule layers consisting of $N,N'$-bis(3-methylphenyl)-$N,N'$-diphenylbenzidine (TPD, 135 nm) and $Alq_3$ (65 nm) are depicted in Fig. 5. In all devices, the cathode is formed by an aluminum layer (thickness 150 nm). To avoid metal contamination of the organic evaporation system, organic and insulating layers were deposited in the same vacuum system, whereas metal layers were deposited separately. Sample handling and device evaluation was performed under dried argon atmosphere. Independent from the active organic material adjacent to the LiF layer, a maximum in efficiency and a minimum in operating voltage can be seen at a LiF layer thickness of 0.5 nm. In our experiments, OLEDs with insulating layers also showed an increased operating lifetime. This is mostly due to the top layer of non-reactive high work function metals like aluminum, which form uniform, non-corrosive films and protect the organic layers beneath.

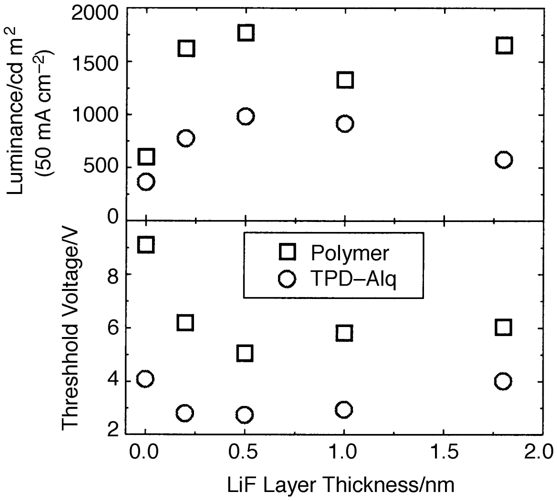

**Fig. 5** Device efficiencies (upper part) and onset voltages (lower part) for fluorene-based (FETP) polymer OLEDs and of devices consisting of small functional molecules. The cathodes consist of a thin insulating layer of LiF and 150 nm Al. The LiF layer thickness is varied.

## Conclusions

In our experiments with polymer OLEDs and with devices based on small functional molecules, we studied the impact of charge carrier injection optimization on device efficiency and lifetime. Injection of positive charge carriers into the electroluminescent layer can be increased by appropriate treatment of the ITO substrate by solvent cleaning in combination with reactive ion etching, and by multi-layer hole transporting structures. Both electron injection and device stability under display operating conditions can be improved by an adequate choice of the cathode material. Binary alloy cathodes or thin insulating layers between the cathode metal and the adjacent organic electron transporting layer reduce sensitivity to oxygen and moisture and, concomitantly, improve device efficiency.

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