Impact of ionic mobility on the performances of iTMC-based light-emitting electrochemical cells

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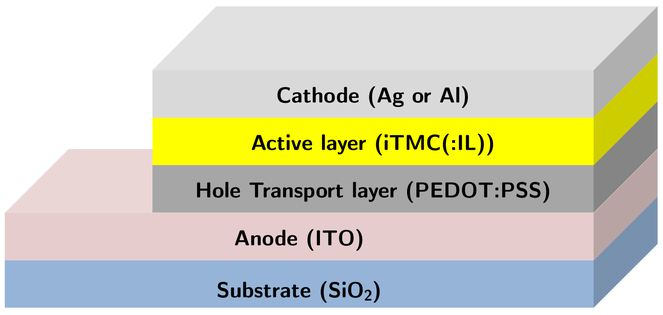
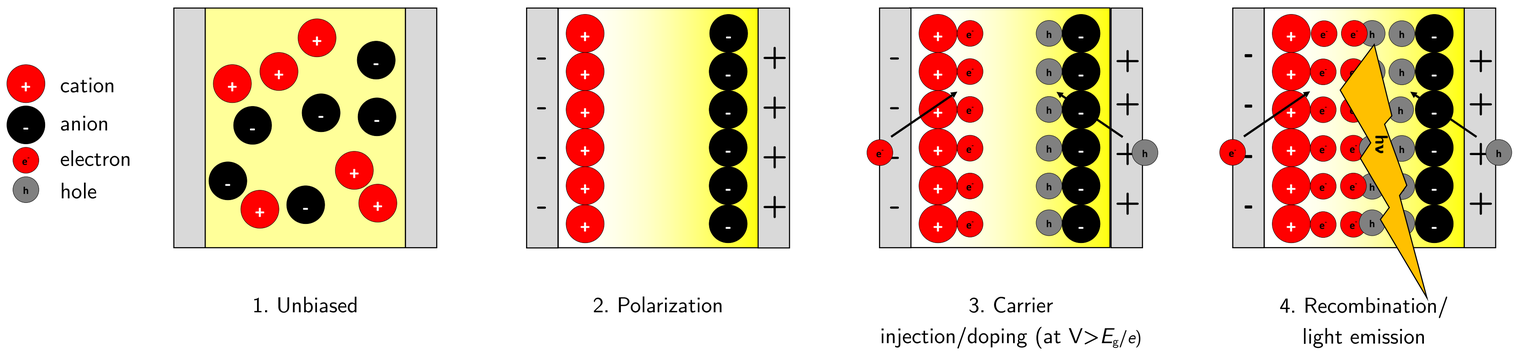
LECs: structure



LECs: working principle



Advantages of LECs:

Simple structure and easy fabrication (cheapness). No need for low-WF highly-reactive metal cathode (insensitivity to air/humidity).

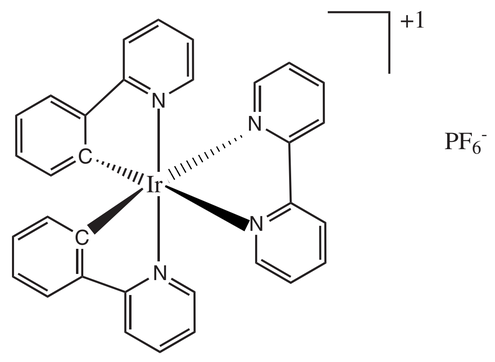
Disadvantages of LECs:

iTMC LECs usually show *long turn-on time*, due to low ionic mobility. On the other hand, faster growing doped zones imply a lower device stability, as they act as *exciton quenchers*: there is a tradeoff between turn-on speed and lifetime. *Ionic mobility* is thus a key parameter.

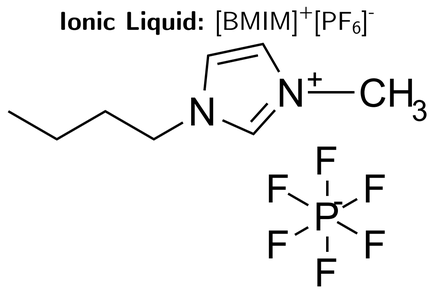
Here we compare the efficiency/lifetime and the electrical behavior of iTMC LECs based on the same electroluminescent Ir(III) complex but with different ionic concentration, being one of them added with an ionic liquid (IL).

Experimental details:

Electroluminescent complex: $[Ir(ppy)_2bpy]^+[PF_6]^-$



Ionic Liquid: $[BMIM]^+[PF_6]^-$



Devices:

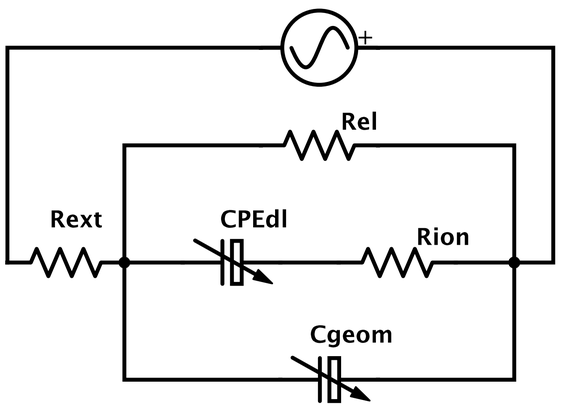
- Anode: pre-patterned ITO (15-20 Ω $\square^{-1}$) (on glass substrate).
- PEDOT:PSS layer: 80 nm (spin coating).
- EL layer: 80-90 nm (s. c. from 20 mg/ml acetonitrile solution).
- Cathode: Al, 70 nm (physical vapor deposition).
- Device area: 0.088 cm^2.

Efficiency/lifetime measurements:

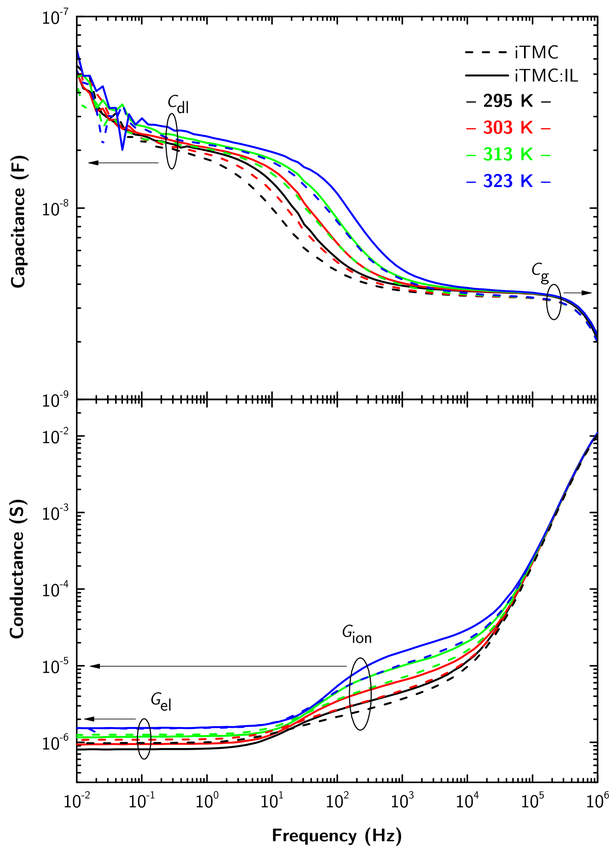
- BoTest "OLED Lifetime Testing System".
- Constant voltage device driving (3V DC).

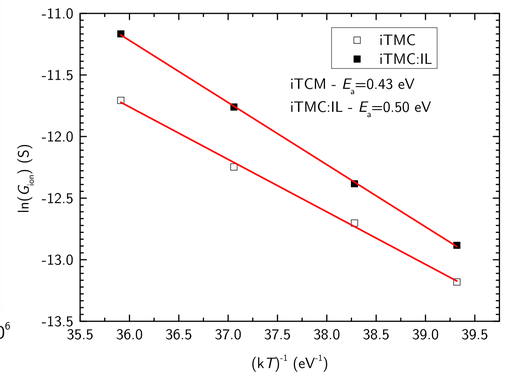
Impedance Measurement:

- Gamry "Interface 1000" Potentiostat.
- 30 mV AC (rms), 0 V DC bias.
- 10^{-2}-10^6 Hz frequency range.
- Ideal LEC equivalent circuit:



Impedance measurements





The mobility of the ions naturally present in the iTMC and iTMC:IL devices originates the features of the impedance spectra in the 10^2-10^4 Hz range, while the low ν tail in the conductance plot is due to *electronic leakage*.

The high ν capacitance corresponds to the *geometrical capacitance* of the active layer, related to the relative dielectric constant of the iTMC(:IL) complex ($Cg=\varepsilon_0\varepsilon_r A/d$).

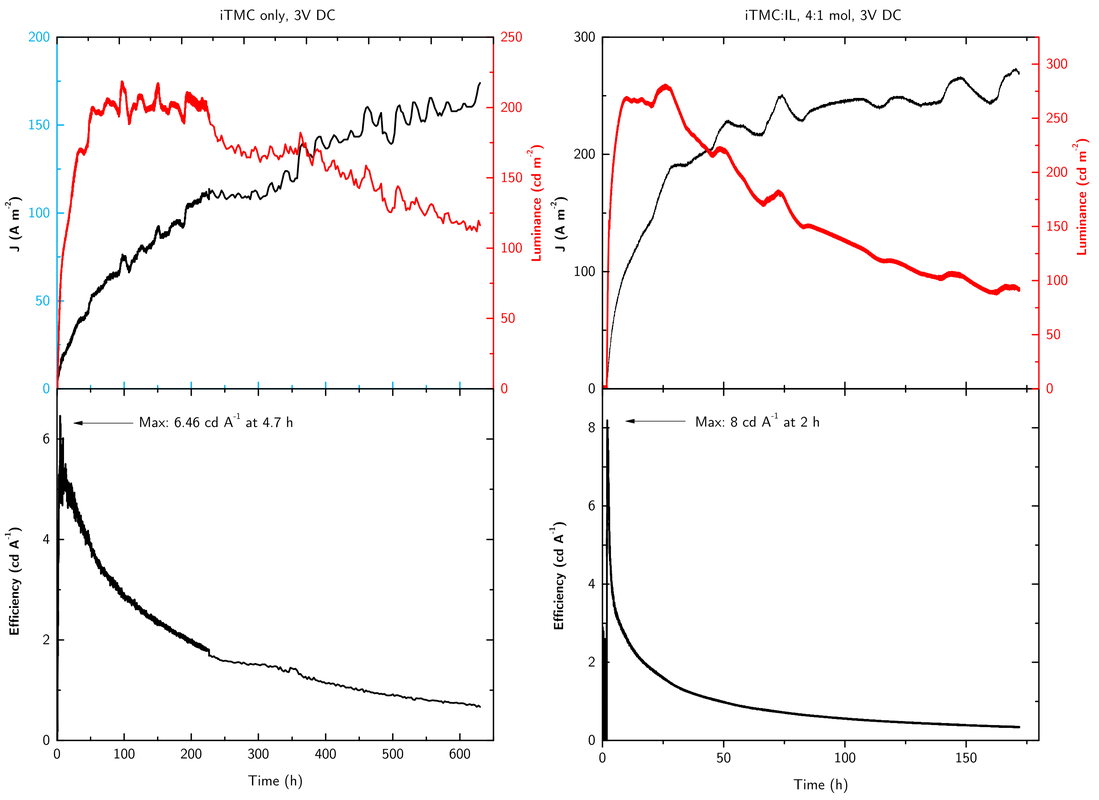
- ◊ The iTMC:IL device has lower electronic leakage and enhanced ionic conductivity, the latter due to the higher density of free PF_6^- anions.
- ◊ The capacitance *plateau* at ν<10 Hz, higher for iTMC:IL, is due to the building of the *electrical double layers*, precursor of the LEC doped zones
- ◊ The ionic mobility increases with temperature.

Quantitative analysis, through the *equivalent circuit* approach, shows that the temperature variation of conductivity obeys an Arrhenius law of the form:

$$\sigma_{ion} = \sigma_0 \exp\left(-E_a / kT\right)$$

The ions thus "hop" through adjacent sites with an activation energy E_a that is slightly lower in the case of the iTMC-only device.

Efficiency/lifetime measurements



While the two devices show similar behavior, their absolute performances are very different:

- ◊ The iTMC:IL device is 4 time faster in reaching the maximum luminance: t_{max}(iTMC) ≈ 4·t_{max}(iTMC:IL) ≈ 100 h.
- ◊ The luminance decays much faster for the iTMC:IL device: $t_{1/2}$(iTMC) ≈ 6.5·$t_{1/2}$(iTMC:IL) ≈ 100 h (reduced lifetime).
- ◊ The current density is higher and grows faster for the iTMC:IL device.
- ◊ Both the maximum luminance and the maximum efficiency improve when IL is added.

The above effects are probably due to the doped zones growing faster in the iTMC:IL case, thus improving the carrier injection and transport towards the intrinsic zone. On the other hand, it is still unclear why the luminance increases when IL is added, even if this could be ascribed to a more symmetrical geometry of the doped zone due to the presence of free ions from the IL.

Conclusions and further investigations:

The addition of free ions to the active layer of an iTMC LEC has a clear beneficial effect on the performances of the device. The downside is a significant reduction of the device lifetime. Avoiding this problem will be the object of future studies. Further experiments are also planned to study the behavior of iTMC:IL LECs based on different complexes/ionic liquids. Improvements in the LECs performances are expected when lighter anions are used in the active film. Anyway, for some of the aforementioned complexes side reactions at the electrodes and/or crystallization of the active layer can not be excluded. These effects would affect both the performances and the lifetime of the devices for reasons not directly related to the ionic size or mass; they would show up as deviations from the ideal LEC circuit behavior and unexpected peaks in X-ray diffraction spectra.

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