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REVIEW

## Illuminating the Electrolyte in Light-Emitting Electrochemical Cells

J. Mindemark<sup>a,b</sup> and L. Edman<sup>a</sup>

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Light-emitting electrochemical cells (LECs) convert electric current to light within an active material comprising an electroluminescent organic semiconductor and an electrolyte. It is well established that it is the presence of this electrolyte that enabled the recent development of low-cost fabrication methods of functional LECs as well as the realisation of unique device architectures. At the same time, it should be acknowledged that the current lower performance of LECs in comparison to the more commonplace organic light-emitting diode, at least in part, is intimately linked to the utilisation of non-ideal electrolytes. In this review, we present the tasks that the electrolyte should fulfil during the various stages of LEC operation, and how the characteristics of the electrolyte can affect the LEC performance, specifically the turn-on time, the efficiency and the operational stability. We thereafter introduce the different classes of electrolytes that have been implemented in LEC devices up to date, and discuss how these electrolytes have been able to meet the specific requirements of the LEC technology.

### 1 Introduction

The light-emitting electrochemical cell (LEC) is an emissive thin-film technology that features several attractive opportunities, including the possibility for low-cost processing using high-throughput solution-based fabrication under ambient air,<sup>1</sup> the realization of stretchable devices,<sup>2, 3</sup> and the introduction of light emission on complex, non-flat and/or unconventional substrates.<sup>4-7</sup> The LEC comprises an intimate blend of an electrolyte and an electroluminescent organic semiconductor as the active material sandwiched between two electrodes. The electrolyte is herein defined as comprising mobile ions and, when necessary, an ion-dissolving and ion-transporting compound; the latter is termed the 'ion transporter'. The electroluminescent organic semiconductor can either be a conjugated polymer (CP),<sup>8-10</sup> a conjugated small molecule,<sup>11-14</sup> or an ionic transition metal complex (ITMC),<sup>15-19</sup> but for the sake of simplicity we have in this review primarily focused on CPs; many of the conclusions should, however, apply to the other materials systems as well.

Importantly, it is the electrolyte that enables the unique properties and potential of the LEC technology, and also clearly distinguishes it from other emissive technologies, such as the organic light-emitting diode (OLED).<sup>20</sup> At the same time, it should be acknowledged that it is the same electrolyte that is the direct or indirect cause to the currently lower performance of LECs in comparison to state-of-the-art OLEDs. For many years, the understanding of the role of the electrolyte in LEC operation was rather rudimentary, and the

tested materials were limited to those developed for other applications, such as lithium-ion batteries. However, with a better understanding of the specifics of LEC operation and the requirements on the electrolyte, it has become clear that high-performance LEC electrolytes should feature a set of distinct, and in some cases unique, properties, which motivate a dedicated design and synthesis. We begin this review by describing how the electrolyte controls the performance of LEC devices in section 2, and thereafter in section 3 we introduce the main groups of employed electrolytes and their functionality with regards to attained LEC operation.

### 2 The drawbacks and benefits of the LEC electrolyte

#### 2.1 The device operation

The LEC is an electrochemical device and as such its operation under applied bias is characterised by an initial ion drift process, which results in the formation of electric double layers (EDLs) at the two electrode–active interfaces. In a well-designed and functional LEC biased at a voltage equal to, or exceeding, the energy-gap potential of the electroluminescent organic semiconductor ( $V \geq E_g / e$ ), the EDLs eliminate the need for an energetic matching of the work function of the injecting electrode with the accepting energy level in the organic semiconductor (as is commonly the case for OLEDs). The first manifestations of the ITMC-LEC and the CP-LEC were distinguished by that the former only comprised one mobile ion, being the anion, whereas the latter comprised mobile anions and cations. This has the consequence that the EDL structure at the cathodic interface in such a single-component ITMC-LEC is set by the distribution of the immobile cations in the pristine and non-biased active material, and that the

<sup>a</sup>The Organic Photonics and Electronics Group, Department of Physics, Umeå University, SE-901 87 Umeå, Sweden

<sup>b</sup>Department of Chemistry – Ångström Laboratory, Uppsala University, Sweden

electron injection in such a device therefore can be somewhat hindered. In more recent manifestations of the ITMC-LEC, it has been a common procedure to add a significant amount of an ionic liquid (with mobile anions and cations) to the active material, so that this issue becomes void.<sup>21, 22</sup>

A long-term discussion has been focussed on what happens after the EDL formation; or more specifically on whether the organic semiconductor becomes electrochemically doped or not. Recent results have, however, demonstrated that in a functional LEC, that is forming effective EDL structures at both electrode interfaces, electrochemical doping does take place.<sup>23</sup> This doping process comprises two key steps: (i) electron/hole injection through the EDL into an available energy level of the organic semiconductor, (ii) ion redistribution to electrostatically 'neutralise' the correspondingly created electronic space charge. At the anode, holes are injected into the HOMO level of the organic semiconductor, and these holes are electrostatically compensated by negative anions; this process is termed *p*-type doping. At the cathode, electrons are injected into the LUMO level and thereafter compensated by cations in a process termed *n*-type doping. With time, these doping regions grow in size, and after a 'turn-on time' a *p-n* junction has formed at their meeting point in the active material. Subsequently injected holes and electrons migrate through the highly conducting doped regions, before recombining at the *p-n* junction under the formation of excitons. It is notable that the formation of a *p-n* junction assures an efficient and balanced injection of holes and electrons. The excitons can subsequently decay radiatively under the emission of photons, which are coupled out of the device structure through a transparent electrode (and substrate).

Another appealing feature that can be enabled by the presence of an electrolyte in LECs is the possibility of attaining broadband emission of white light from a single-component emitter. In an early study, it was reported that the phase separation between the light-emitting compound and the electrolyte could result in a broadening of the emission spectrum from the device.<sup>24</sup> White light emission has also been reported from a multifluorophoric copolymer. In this case, the electrolyte acted to physically separate the fluorophores within different polymer chains, thereby limiting the exciton energy transfer from high- to low-energy fluorophores.<sup>25</sup> In ITMC-LECs, a similar electrolyte-induced spatial separation of the emissive species has been observed to lead to a blue-shift of the emitted light.<sup>26</sup>

## 2.2 The device performance

Up to this point, the electrolyte has been demonstrated to represent a positive influence on the device function, as it notably results in efficient and balanced electron/hole injection and allows for a low-cost solution-based fabrication process using air-stable materials. It is, however, important to point out that the electrolyte also brings with it a number of challenges, and that an LEC in many cases features a lower performance than, for instance, a corresponding OLED. In this

section we analyse the effects of the electrolyte on the LEC performance, with a focus on three important performance parameters: turn-on time, efficiency, and operational lifetime.

**2.2.1 The turn-on time.** As both the initial EDL and the subsequent *p-n* junction formation processes are dependent on an ionic redistribution, the turn-on time to significant brightness of an LEC is dependent on the ionic conductivity of the active material ( $\sigma_{\text{ion}}$ ), as well as the driving voltage and the active material thickness. In an electrolyte with fully dissociated ions, the former is defined by the following equation:

$$\sigma_{\text{ion}} = \sum c_i q_i \mu_i \quad (1)$$

where  $c_i$  is the concentration,  $q_i$  the charge, and  $\mu_i$  the mobility of each ion. Since the mobility of bulky ions is typically significantly lower than that of the electronic charge carriers, and since there is an upper practical and desired limit for the ionic concentration (more on this topic later on), the LEC turn-on time is slower than that of OLEDs, with reported values being in the range of a few tenths of a second to several hours.<sup>27-30</sup> This effectively eliminates LECs from fast-response applications, such as video displays, although efforts into stabilisation of a pre-formed ion structure, and concomitant doping structure, through chemical fixation<sup>31</sup> or a lowering of the operational temperature<sup>32</sup> could result in 'static-junction' LECs that could become useful for such applications as well. In addition to fast response, such ion-stabilised devices have the potential to also alleviate other electrolyte-related issues of LECs with concomitant improvements in device stability.<sup>32-34</sup> Nevertheless, for conventional LECs it is motivated to improve upon the ionic conductivity, primarily *via* improved ion mobility (see Eq. 1), in order to attain a practical dynamic response. This is particularly true for ITMC-LECs, for which the immobility of the bulky cationic complexes leads to very slow turn-on kinetics. In such devices, a second electrolyte (often an ionic liquid) is commonly added to the active material to reduce the turn-on time to practical levels.<sup>37</sup>

In the context of CP-LECs, it can be a complicating issue that the active material commonly features a significant *phase separation* between a hydrophobic electroluminescent organic semiconductor and a hydrophilic electrolyte, or *vice versa*, as visualised in the micrographs presented in Fig. 1.<sup>38</sup> Considering that the long-range ion transport during device turn-on most likely takes place within the electrolyte phase, a too severe phase separation might lead to unnecessarily long, tortuous or even blocked transport pathways for the ions, resulting in a low effective mobility and a slow turn-on time. The common use of high-molecular-weight polymer electrolytes in CP-based LECs will inevitably lead to such a phase separation since the mixing of different polymers is an entropically unfavourable process.<sup>39</sup> The phase separation can also be further amplified by the use of solvent mixtures in the active-material ink, where preferential evaporation of the more volatile component may cause precipitation of the component that is less soluble in the higher-boiling-point solvent,<sup>4</sup> and, more severely, by the high operational temperatures that can result from high-brightness operation.

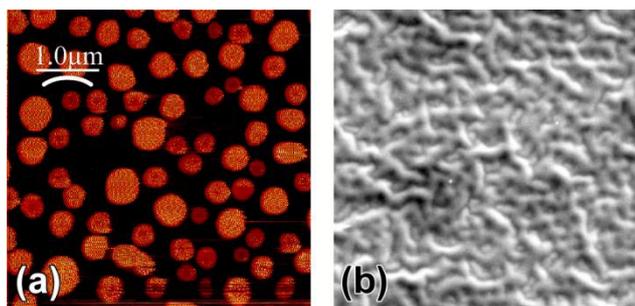


Fig. 1 (a) Electric force microscopy image illustrating the phase separation in an active material comprising a blend of a CP and an ionic liquid electrolyte. Reprinted (adapted) with permission from ref. <sup>35</sup>. Copyright 2006 American Chemical Society. (b) A (23 μm×23 μm) scanning electron microscopy image showing the phase-separated surface morphology of an active material comprising a blend of a CP and crown ether-based electrolyte. Adapted with permission from ref. <sup>36</sup>. © 2004 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Cao *et al.* addressed the issue of phase separation through the addition of a non-ionic surfactant to the active material, which resulted in the formation and stabilisation of a bicontinuous network morphology, and a drastically improved turn-on time.<sup>40</sup> It should, however, be noted that the addition of a large amount of surfactant also can have a plasticising effect with concomitantly improved ion mobility,<sup>41</sup> and that Wegh *et al.* included the same surfactant in another active material system without improvements in device performance.<sup>42</sup>

Recent results further indicate that the doping process, and thus the device turn-on, also depends on the dynamics at the interfaces between the electrolyte and the organic semiconductor, and that, *e.g.*, the interaction between the ions and their ion transporter can play a key role for the device kinetics. In Fig. 2 such a scenario is presented, where the cation is solvated by an ion transporter in the electrolyte phase, but liberated from this ion transporter before participating in doping in the organic semiconductor phase. By designing electrolytes that take this effect into account, much improved turn-on times have been attained.<sup>43</sup>

**2.2.2 The efficiency.** For quite some time, very little, if any, attention was paid on controlling the doping structure in LECs, even though the direct correlation between doping structure and device efficiency is well established and understood in similar *p-n* junction devices based on organic and inorganic semiconductors.<sup>44, 45</sup> An important tool for this end did, however, emerge from the insight that the ion concentration in the pristine active material of LECs, as determined during the ink preparation, effectively controls the (average) doping concentration in a device operating at steady state.<sup>46, 47</sup> Alternatively formulated, each doping event ‘consumes’ one ion, and when all ions in the active material are locked up, no further doping can take place. Fang and coworkers executed a number of systematic studies on this topic, where they showed that the width of the *p-n* junction in open planar devices,<sup>47</sup> as well as the efficiency and stability of sandwich devices,<sup>46</sup> is strongly dependent on the selected ion concentration.

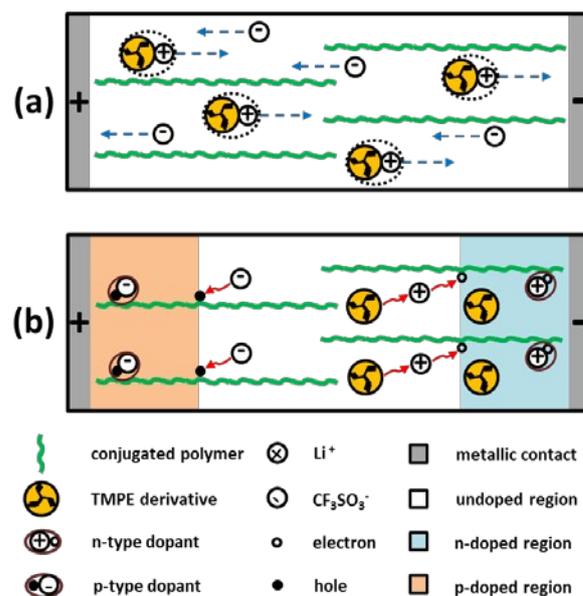


Fig. 2 Schematic illustrating the various processes in effect during LEC turn-on. (a) The initial drift of ions within the electrolyte phase, with ‘free’ anions drifting towards the positive anode, and the solvent-coordinated cations drifting towards the negative cathode. (b) The subsequent electrochemical doping of the organic semiconductor, highlighting the ion ingress into the light-emitting semiconductor phase. Note that the cation is proposed to be released from its solvating molecule before the doping event. Reprinted with permission from ref. <sup>43</sup>. Copyright 2014 American Chemical Society.

One conclusion from these early studies was that the electrolyte concentration in previously studied LEC systems frequently had been way too high, presumably as these aimed for achieving a fast turn-on time and since they were inspired by the high ion concentration employed in other electrochemical devices, such as batteries and electrochromics. In an early study, the attained improved device performance was attributed to a suppression of side reactions when the effective width of the *p-n* junction was increased at lower electrolyte loadings.<sup>46</sup> Later studies have demonstrated that a lower doping concentration in addition will suppress doping-induced exciton quenching<sup>48</sup> and self-absorption,<sup>49, 50</sup> with the result being that a much improved conversion efficiency from electrical input to light output could be attained in such electrolyte-optimised devices.<sup>46</sup>

**2.2.3 The operational lifetime.** The doping-induced quenching reactions discussed in the previous section will not only limit the device efficiency, but can also result in chemical side reactions as well as severe self-heating. Such events will have an obvious negative influence on the device stability, but with the introduction of more doping-optimised LECs these side reactions are suppressed and the operational lifetime have accordingly been improved significantly, although it still lags behind that of OLEDs based on the same electroluminescent organic semiconductor. This shortcoming can, at least partially, be attributed to the limited stability of the electrolyte itself. The electrochemical stability window (ESW) of a compound is defined by its onset potentials for oxidation and reduction (as established with, *e.g.*, cyclic voltammetry), and the ESW of the

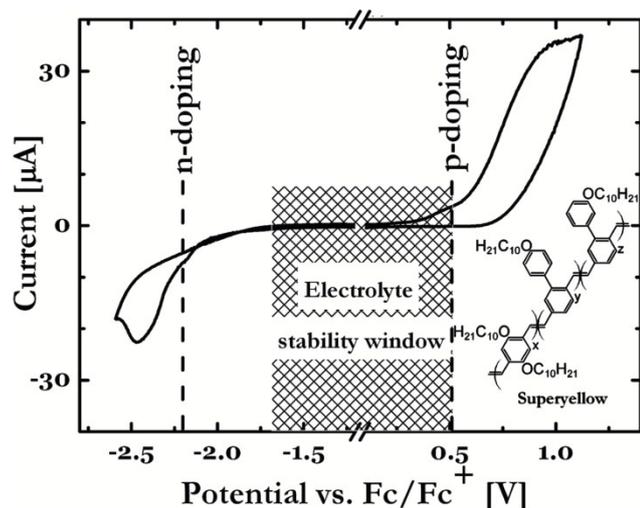


Fig. 3. CV data illustrating the limited electrochemical stability window of a PEO:KCF<sub>3</sub>SO<sub>3</sub> electrolyte in comparison to the *p*- and *n*-type doping potentials of the conjugated polymer Super Yellow. Reprinted with permission from ref. <sup>52</sup>. Copyright 2010, AIP Publishing LLC.

electrolyte in a stable LEC should preferably be situated within the boundaries defined by the *n*-type and *p*-type doping potentials of the organic semiconductor in order to minimise the risks for electrolyte-induced side reactions.<sup>51</sup>

However, in a majority of the LEC systems investigated thus far, the *n*-type doping (reduction) of the organic semiconductor is located at a larger negative potential than the reduction potential of the electrolyte (see Fig. 3), with a consequence being that the thermodynamically preferred cathodic reaction is an *electrochemical side reaction* involving the electrolyte.<sup>51</sup> This is actually akin to the situation in Li-ion batteries, where electrolyte reduction at the anode (during battery discharge, the anode is the negative electrode) can be a limiting factor for the device lifetime. In the case of Li-ion batteries, this is mitigated by the *in situ* formation of a stable protective solid electrolyte interphase layer that protects the electrolyte as well as the electrode from further degradation.<sup>53</sup> In an LEC, however, the formation of an insulating degradation layer at an electrode interface is effectively a disaster, as the device operation is dependent on electronic contact between

the electrode and the active material.<sup>43, 51</sup> Moreover, a delay in the onset of *n*-type doping caused by these electrochemical side reactions will result in that the light-emitting junction is formed off-centre closer to the cathode,<sup>51</sup> which in turn can result in electrode-quenching of the light emission and the formation of microshorts.<sup>54</sup> We also note that for organic semiconductors with their energy levels shifted in the cathodic direction, similar side reactions are observed at the anodic interface.<sup>55</sup>

An interesting observation in this context is that the LEC doping process can become kinetically favoured at a higher drive voltage. Thus, by driving the device with a high prebias during the turn-on process, when the *p*-*n* junction is formed, the electrolyte-induced side reactions can be effectively suppressed, whereafter the applied bias is lowered to the appropriate level for long-term operation. This voltage protocol can be conveniently effectuated by driving the device at constant current (galvanostatic mode), as the resistance of the active material will decrease during the doping process.<sup>46, 52</sup>

Nevertheless, while this offers some temporary relief, a more long-term solution to the electrolyte stability problem would involve the design and synthesis of electrolytes with expanded ESWs, particularly on the cathodic side.<sup>56</sup>

We also note that phase separation can lead to the formation of electrolyte-rich and electrolyte-poor regions, so that the active material will not have the same ion concentration throughout. In such a system, areas with high ion concentration will turn on more quickly, but also burn out more quickly, than the rest of the active material.<sup>57</sup> In systems with a large phase separation, it is further conceivable that efficient carrier injection and doping might be confined to the interfaces between electrolyte-rich and CP-rich regions.<sup>35, 58</sup>

### 3 The electrolyte systems

#### 3.1 PEO-based electrolytes

In the pioneering LEC study by Pei *et al.*, the electrolyte consisted of the alkali metal salt LiCF<sub>3</sub>SO<sub>3</sub> dissolved in the ion-transporting polymer poly(ethylene oxide) (PEO).<sup>8</sup> The PEO was demonstrated to enable significant ionic mobility (by

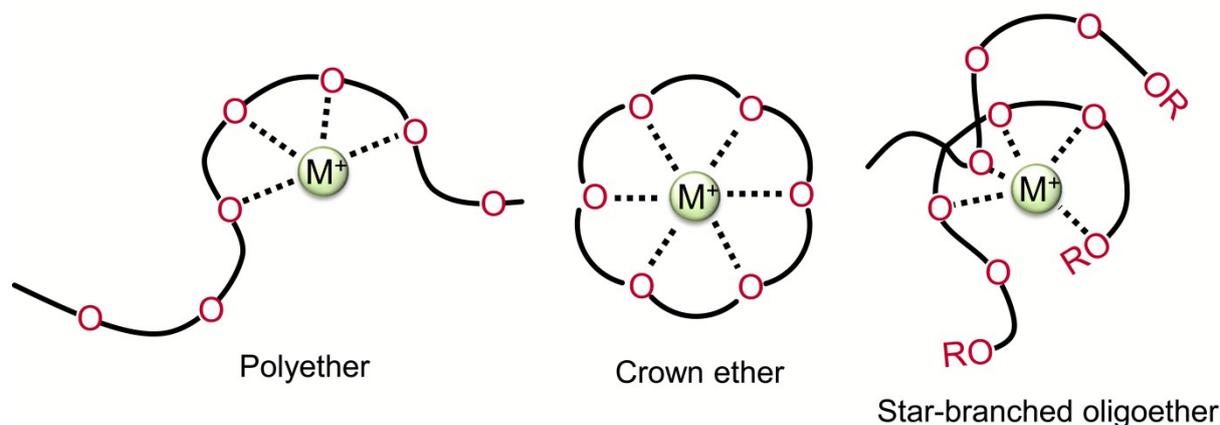


Fig. 4 A schematic illustration of the structure and cation coordination of representative ether-based ion transporters. For the star-branched oligoether to the right, R represents the end-group, which can be a hydrogen or a methyl group.

solvating the cations and providing ionic transport paths as illustrated in the left portion of Fig. 4), without which the device behaviour becomes sluggish with a long turn-on time to light emission.<sup>8</sup> Conversely, without the salt, the device behaved as a poor OLED requiring a high turn-on voltage for light emission.<sup>9</sup> The PEO-based electrolyte was presumably imported from the energy storage field, where such solid-state electrolytes have been extensively investigated since the late 1970s, primarily for use in solid-state Li batteries.<sup>59-62</sup> As it turns out, PEO is a decent but not perfect ion-transporting material for LECs as well, and much of the subsequent LEC research has utilised PEO-based electrolytes.

One often highlighted issue with PEO-based electrolytes in other applications has been their propensity for crystallisation at room temperature. PEO is a semicrystalline polymer with a melting temperature of  $\approx 60^\circ\text{C}$ , and it forms high-melting crystalline complexes with many salts. Since it has been demonstrated that ion transport almost exclusively takes place in the amorphous PEO regions (and above the glass transition temperature),<sup>63</sup> such crystallisation often limits the practical operational temperature of the corresponding devices to be above the melting point of the electrolyte, *i.e.* above room temperature.<sup>64</sup> Heating of planar LEC devices above the melting point of the PEO-based electrolyte has accordingly been reported to result in a markedly reduced turn-on time and voltage.<sup>64, 65</sup>

The crystallisation of a polymer from its molten state is typically highly dependent on the cooling rate, and this behaviour has been demonstrated for PEO-based electrolytes as well.<sup>64</sup> A proper heat treatment can then suppress the crystallinity of the electrolyte by 'freezing' the material in a metastable amorphous phase. Such a combination of thermal annealing at temperatures between 330 and 400 K and subsequent quenching was used by Alem *et al.* to attain an amorphous PEO-based electrolyte phase at ambient temperature.<sup>66</sup> This treatment did as expected result in a notably improved turn-on time and an increase in the emission intensity for planar LEC devices. While these results are educational, the resulting amorphous morphology is thermodynamically unstable, which renders it susceptible to

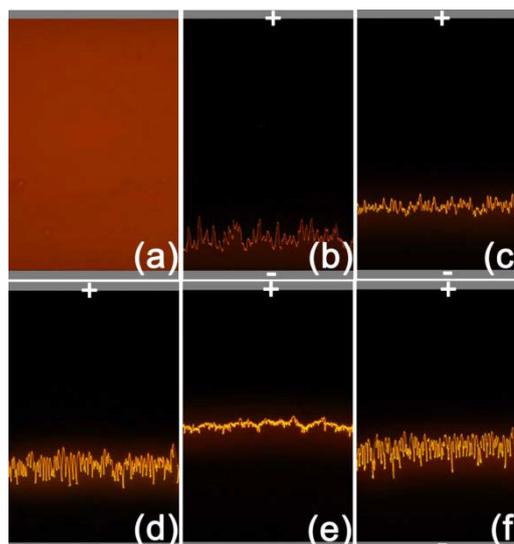


Fig. 5 Photographs of the light-emitting *p-n* junction in planar Al/(MEH-PPV + PEO + MClO<sub>4</sub>)/Al LEC devices, with different cations: (a) M = Li, image taken before application of voltage; (b) M = Li; (c) M = Na; (d) M = K; (e) M = Rb; (f) M = Cs. The photographs were recorded under UV illumination at 340 K under 800 V bias. Reprinted with permission from ref.<sup>69</sup>. Copyright 2006, AIP Publishing LLC.

crystallisation over time, particularly if the corresponding device is operated at elevated temperatures as can be induced by, *e.g.* self-heating effects.<sup>34, 67, 68</sup> We also note that the existence of microscopic crystalline domains in PEO-based active materials have been suggested to lead to light emission loss by light scattering in sandwich LECs.<sup>49</sup>

Li-based salts have been the common choice for the salt in PEO-based electrolytes in LECs, again presumably since the first scientists in the LEC field were inspired by the concomitant successful research and development in the field of Li batteries. However, in several LEC studies it has been shown that the employment of other cations than Li results in that the light-emitting *p-n* junction will be moved away from the cathode and be more centred, which is desirable as it will effectively eliminate undesirable electrode quenching effects.<sup>70</sup> For a series of MClO<sub>4</sub> salts (*M* = Li, K, Na, Cs, Rb), Hu

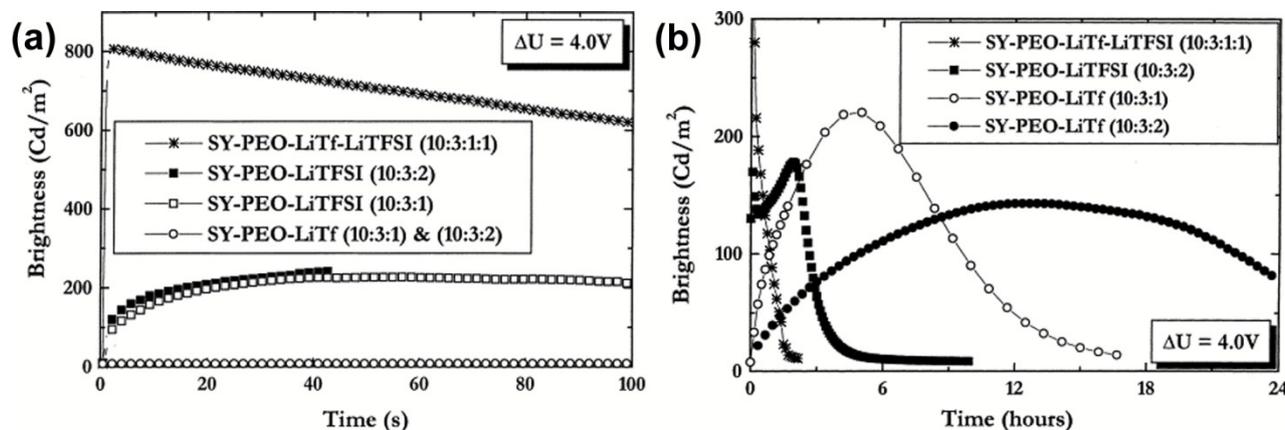


Fig. 6 (a) Turn-on kinetics and (b) long-term stability of LECs based on the conjugated polymer Super Yellow (SY) and a PEO:LiX electrolyte (*X* = Tf, TFSI, Tf + TFSI). Reprinted from Synthetic Metals, 138, L. Edman, D. Moses, A. J. Heeger, Influence of the anion on the kinetics and stability of a light-emitting electrochemical cell, 441–446, Copyright 2003, with permission from Elsevier.<sup>28</sup>

and Gao found that the use of larger cations invariably led to the light-emitting *p-n* junction being more centred and more strongly emitting than for the device comprising the Li salt; see Fig. 5.<sup>69</sup> Similar results were obtained by Shin *et al.*, who studied the effects of the cation for  $MCF_3SO_3$  ( $M = Li, K, Rb$ ) salts and reported a more centred and brighter *p-n* junction as well as faster turn-on for devices with  $M = K$  and  $Rb$  compared to  $M = Li$ .<sup>64, 71</sup> The faster turn-on time for devices comprising the larger cation might seem counterintuitive, but it has been demonstrated that for PEO: $MCF_3SO_3$  electrolytes the ionic conductivity increases with increasing cation size.<sup>72</sup>

Another parameter to play with is the selection of the anion.<sup>49, 50</sup> By replacing the  $CF_3SO_3$  (Tf) anion with a larger  $N(CF_3SO_2)_2$  (TFSI) anion in a PEO:LiX electrolyte, a markedly faster turn-on for sandwich cells was achieved, as shown in Fig. 6(a). The LiTFSI salt was in part developed for suppressing the room temperature crystallinity of the corresponding PEO-based electrolytes and thereby attaining a higher ionic conductivity;<sup>73</sup> the observed improvement in the turn-on kinetics could thus be attributed to a reduced crystallinity of the electrolyte phase.<sup>28</sup> The fastest turn-on in Fig. 6(a) was attained by using a combination of both the Tf and the TFSI anions, and it is plausible that this mixed electrolyte featured an even lower degree of crystallinity at room temperature, presumably since the combination of two anions makes the crystallisation of the electrolyte kinetically hindered.

A drawback with these alternative, less crystalline electrolytes was that the long-term stability suffered, as illustrated in Fig. 6(b).<sup>28</sup> This drawback was attributed to the lower cathodic stability of the TFSI anion in comparison to the Tf anion, implying that the preferred cathodic reaction is reduction of the TFSI anion and not *n*-type doping of the conjugated polymer, in line with the discussion in section 2.2.3 above. Polyatomic anions, such as Tf and TFSI, have considerable electron affinity by virtue of their notably electron-withdrawing substituents. While this leads to favourable ion dissociation and high ionic mobility, it also makes the ions more susceptible to reduction, with TFSI, bearing the larger number of electron-withdrawing substituents, being less stable towards reduction than Tf.<sup>28, 74</sup>

### 3.2 Linear oligoether-based electrolytes

The move from polyethers to oligoethers as the ionic transporter in LECs can be motivated by a number of arguments. First, the phase separation that is highly prominent due to entropic reasons in active materials comprising two or more polymers, *e.g.* PEO and a conjugated polymer, will become less of an issue when the high-molecular-weight ion transporter is replaced by a lower-molecular-weight counterpart. Second, the stronger influence of symmetry-breaking and free volume-inducing end-groups in short-chain molecules can be utilised for the attainment of reduced

crystallinity and/or a depression of the melting point.<sup>75</sup> Third, the glass transition temperature ( $T_g$ ) of a macromolecular compound (at which its dynamic properties change drastically) is inversely related to its molecular weight, as described by the Flory–Fox equation, implying that an oligomeric ion transporter will feature faster chain dynamics, and a higher ionic conductivity, than its high-molecular-weight equivalent. Moreover, a reduction in molecular weight of the ion transporter will also at some point shift the transport mode from ion movement between different coordination sites on dynamic, but effectively immobile, polymer chains<sup>76, 77</sup> to a *vehicular transport* mechanism, by which (one of) the ions moves together with its solvent molecule(s).<sup>78</sup> With the vehicular transport in effect, it is possible to have the emission zone cleared from both ion transporter molecules and ions at steady-state,<sup>56</sup> which effectively can eliminate detrimental interactions between the electrolyte and the excitons.<sup>46</sup> Linear low-molecular-weight PEO analogues are the simplest and most straightforward embodiment of oligoethers, but this group of compounds has only been explored to a limited extent in LECs. Yu *et al.* fabricated LECs comprising a dimethyl ether end-capped oligoethylene oxide (OEO-DME; molecular weight =  $1000 \text{ g mol}^{-1}$ ) blended with  $LiCF_3SO_3$  salt as the electrolyte. In line with the expected improved ionic conductivity of the oligoether–salt complex, the OEO-DME-based LECs displayed faster turn-on kinetics than corresponding PEO-based devices.<sup>79</sup> Ion-transporting linear oligoethers can also be introduced as side chains grafted onto a polymer backbone. Wantz *et al.* synthesised a set of random copolymers comprising oligoethyleneoxide methyl ether methacrylate (OEOMMA) and methyl methacrylate (MMA) as the base units. By systematically varying the ratio of these base units, the  $T_g$  of the copolymer could be tailored between  $-65 \text{ }^\circ\text{C}$  (only OEOMMA) and  $115 \text{ }^\circ\text{C}$  (only MMA). LEC devices fabricated with such high- $T_g$  copolymers as the ionic transporter were reported to feature static (or frozen) junction operation at room temperature.<sup>80</sup>

### 3.3 Non-linear oligoether electrolytes

Crown ethers are cyclic oligoethers that are capable of coordinating and solvating metal cations within their open interior as illustrated in the middle portion of Fig. 4.<sup>36, 81</sup> The resulting complex is characterised by a relatively hydrophobic exterior (being the crown ether ring), thereby rendering the corresponding crown ether-based electrolyte more compatible with a hydrophobic light-emitting compound, such as a CP. This has been anticipated to result in decreased phase separation in the active material of LECs.<sup>82</sup> A drawback is, however, that the binding between the chelating crown ether groups and the cation is typically very strong and the resulting complex bulky, which results in poor cation mobility and a low ionic conductivity.<sup>83</sup>

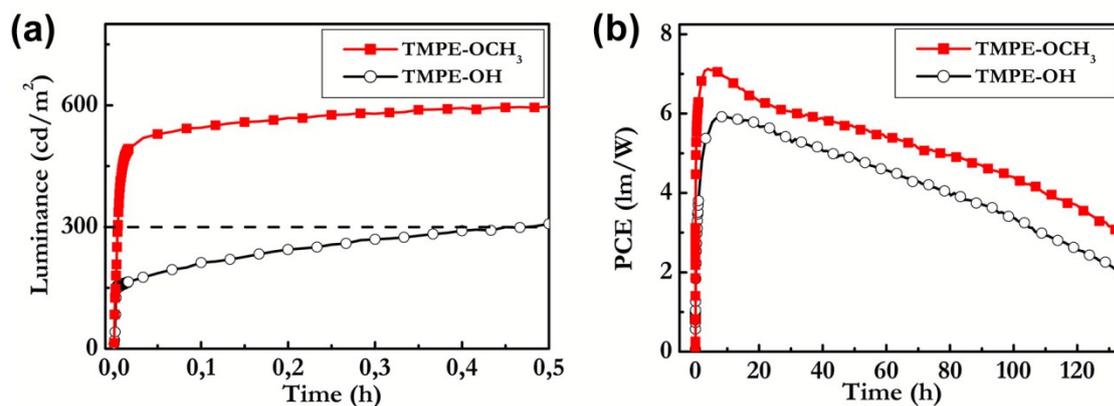


Fig. 7 The turn-on kinetics (a) and the power conversion efficacy (b) of ITO/{SY+TMPE-X+LiCF<sub>3</sub>SO<sub>3</sub>}/Al LECs driven by a current density of 7.7 mA cm<sup>-2</sup>, with X = OCH<sub>3</sub> or OH. Reprinted (adapted) with permission from ref. <sup>43</sup>. Copyright 2014 American Chemical Society.

The initial screening of a range of crown ethers with different Li salts and CPs by Cao *et al.* confirmed the feasibility of crown ether-based electrolytes in LECs, and also singled out the dicyclohexano-substituted 18-crown-6 (DCH-18C6) as the best of the investigated ion transporters with a performance on par with corresponding PEO-based devices.<sup>82</sup> This was rationalised by that the unsubstituted 18C6 crown ether provided a poorer blending capacity with the CP, while an aromatically substituted 18C6 crown ether featured a more rigid ring structure with a concomitantly decreased cation mobility. Later studies demonstrated that the DCH-18C6:LiCF<sub>3</sub>SO<sub>3</sub> electrolyte is crystalline at room temperature, and thus that ambient-temperature static junction operation is possible.<sup>84-86</sup>

A molecular architecture that has recently shown great promise for the ion transporter in LECs is a star-branched oligoether termed trimethylolpropane ethoxylate (TMPE). It features three ion-coordinating oligoether arms grafted onto a trifunctional trimethylolpropane core, as depicted in the right part of Fig. 4. Similar to crown ethers, the size of a typical TMPE molecule is such that it singlehandedly can solvate one cation, thereby facilitating vehicular transport. However, it is important to note that TMPE oligomers, unlike crown ethers, are polydisperse compounds, and that although the 'average' TMPE molecule with a molecular weight of 450 g mol<sup>-1</sup> comprises 2–3 oxyethylene repeating units per arm, the reality is that the arms can contain a wider variety of repeat units.

The end-groups play an important role for the performance of oligomers, and the first study in this field utilised a hydroxyl-capped TMPE termed TMPE-OH, into which the salt LiCF<sub>3</sub>SO<sub>3</sub> was dissolved. An optimised LEC based on this electrolyte featured a respectable operational lifetime of 1150 h at a brightness of >100 cd m<sup>-2</sup> and a high power conversion efficacy (PCE) of 10.2 lm W<sup>-1</sup>. The performance improvement in comparison to corresponding PEO-based LECs was attributed to an expanded ESW, the vehicular transport mechanism that renders the emission zone free from electrolyte at steady-state, and the good phase compatibility between the electrolyte and the emissive conjugated polymer. A persistent drawback with TMPE-OH-based devices is, however, that the turn-on time to significant brightness is very slow at low voltages.<sup>56</sup>

This issue was addressed by methylating the end-group for the synthesis of a methoxy-capped TMPE ion transporter termed TMPE-OCH<sub>3</sub>. Corresponding TMPE-OCH<sub>3</sub>-based LECs featured a much improved turn-on time of 16 s to 100 cd m<sup>-2</sup>, a notably improved PCE as well as a retained long-term stability, as indicated in Fig. 7. The improved turn-on kinetics were rationalised by: (i) an elimination of the hydrogen-bond network present in the TMPE-OH electrolyte, thereby increasing the ion mobility, and (ii) a weakened cation coordination that resulted in a more facile ion release during the initial doping process (see Fig. 2).<sup>43</sup>

### 3.4 Ionic liquids

Up to this point, we have solely covered ether-based ion transporters into which an alkali metal salt is dissolved. Re-occurring setbacks with these electrolytes have been an inadequate ESW (see Fig. 3), a limited ion mobility at room temperature, and issues with phase separation between the hydrophilic electrolyte and a hydrophobic light emitter. Ionic liquids (or 'molten salts') are electrolytes with a low melting point (in some cases below room temperature), which can be hydrophobic, highly conductive, and feature a broad ESW.<sup>87, 88</sup> They do in addition not require an ion transporter for ion solvation and transport, and are a frequent addition to ITMC-LECs to speed up the turn-on kinetics.<sup>21, 37</sup> It thus appears as though ionic liquids could be a good fit for LEC devices based on hydrophobic CPs as well. The first ionic liquids employed in CP-LECs were based on a tetraalkylammonium cation,<sup>29, 35, 54, 89-95</sup> but other ionic-liquid LECs based on imidazolium<sup>90, 96-98</sup> or phosphonium<sup>92, 99</sup> cations have also been investigated. The studied anions include TFSI,<sup>35, 89-93, 99</sup> CF<sub>3</sub>SO<sub>3</sub>,<sup>29, 54, 94, 95</sup> PF<sub>6</sub>,<sup>96</sup> BF<sub>4</sub>,<sup>96</sup> (2,4,4-trimethylpentyl)phosphinate<sup>92</sup> and ethylsulfate,<sup>97</sup> and the chemical structures of two investigated ionic liquids with promising properties are presented in Fig. 8(a).

Quite surprisingly, several early LEC studies reported on a severe phase separation between the ionic liquid and the CP (see Fig. 1(a)), and the device performance was, in fairness, not impressive either.<sup>35, 92, 93, 96</sup> Nevertheless, some success has been attained, as exemplified by that Shin and coworkers demonstrated the first low-voltage operation of a planar LEC with a mm-sized electrode gap, at room temperature by

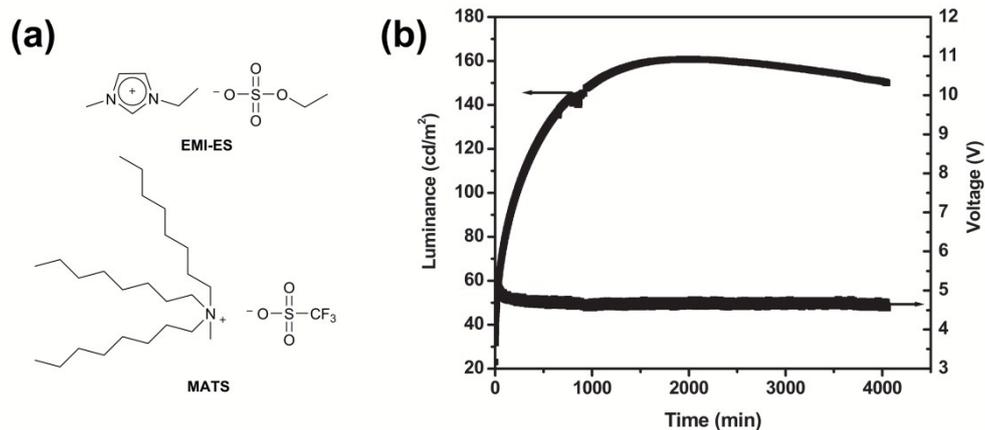


Fig. 8 (a) The chemical structure of the ionic liquids 1-ethyl-3-methylimidazolium ethylsulfate (EMI-ES) and methyltrioctylammonium trifluoromethanesulfonate (MATS). (b) The optoelectronic performance of an LEC comprising the ionic liquid MATS as the electrolyte. Adapted with permission from ref. <sup>29</sup>. © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

employing a 1-ethyl-3-methylimidazolium ethylsulfate (EMI-ES) ionic liquid with a melting temperature below  $-20\text{ }^{\circ}\text{C}$ .<sup>97</sup> Moreover, Shao *et al.* reported a long operational lifetime of several days at significant luminance from sandwich-cell LECs, using methyltrioctylammonium trifluoromethanesulfonate (MATS) as the ionic liquid (see Fig. 8).<sup>29</sup> By including a crosslinked hole-transport layer between the anode and the active layer, the same authors were able to report an even longer operational lifetime in a follow-up study.<sup>95</sup>

### 3.5 Electrolytes with mixed ionic and electronic conductivity

It has been recognised that the issues with phase separation could be effectively and conveniently resolved through the development of a multifunctional compound, which simultaneously features electronic conductivity, ionic conductivity, and electroluminescence. The most studied material group that meets this challenge is the ITMCs,<sup>100</sup> but attempts have also been made with CPs. The first development in the latter aspect constituted the synthesis of CPs endowed with ion-transporting units, but where the ions were provided by the addition of a salt. Examples of such compounds are presented in Fig. 9, and include CPs endowed

with ion-transporting side chains in the form of oligoethers (Fig. 9(a))<sup>24, 27, 101-103</sup> or crown ethers<sup>104</sup> (Fig. 9(b)), or the inclusion of an ion-transporting oligoether block within a conjugated main chain for the formation of a block copolymer (Fig. 9(c)).<sup>105-107</sup>

Pei *et al.* synthesised a polyfluorene derivative equipped with an oligoether side chain that featured an impressive efficiency in LEC devices, but which suffered from a short operational lifetime and slow turn-on kinetics.<sup>24, 27</sup> The latter issue originated in the short length of the ion-transporting chains and the anchoring of these side chains to a stiff conjugated backbone, which makes long-range ion transport between different solvation sites cumbersome. The issue of low ion mobility and a concomitant slow turn-on is also pronounced in block copolymer LECs, where the ion-conducting oligoether blocks are anchored at both ends by stiff conjugated moieties. In several cases, a reasonable turn-on time could be accomplished through the addition of PEO,<sup>24, 74, 104, 108</sup> but then the number of compounds in the active material is back to the original three and issues with phase separation might reappear. An additional disadvantage with the block copolymers is that the intra-chain electronic transport is

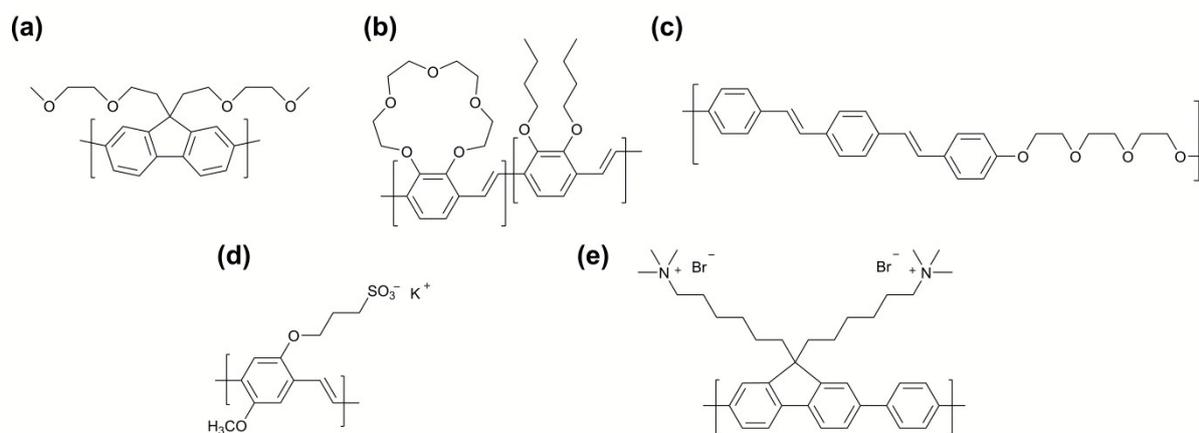


Fig. 9 A conjugated polymer endowed with an ion-transporting side chain comprising either an oligoether (a) or a crown ether (b). A block copolymer comprising conjugated and oligoether repeat units (c). A conjugated polyelectrolyte with a mobile cation (d) or a mobile anion (e).

hindered by the ion transporter blocks, and that long-range electronic motion accordingly relies on, often inefficient, intermolecular transport.

A more elegant route to a hybrid electron and ion conductor within a single material then constitutes the tethering of an ionic group directly onto the CP backbone, which leaves the counterion 'free' and mobile; see Fig. 9(d–e). Such a multifunctional conjugated polyelectrolyte (CPE) bears similarities with the ITMCs, and LEC-functional CPEs with either mobile cations<sup>109, 110</sup> or anions<sup>34, 111–114</sup> have been reported. Contrary to claims otherwise,<sup>109</sup> it is indeed possible to attain both *n*- and *p*-type doping in a system with only one type of ion being mobile, since ion migration towards one electrode for *n*-/*p*-type doping will leave an uncompensated immobile counterion in the region next to the other electrode, where it can take part in the balancing *p*-/*n*-type doping process.<sup>34, 115, 116</sup> While there is ample room for variation of the conjugated backbone and the mobile counterion, there is a limited number of ionic moieties that can be coupled to the backbone in a synthetically practical way. In the reported CPE structures, the tethered cation is exclusively alkyltrimethylammonium (Fig. 9e)<sup>34, 111–113</sup> while the tethered anion is invariably the sulfonate (Fig. 9(d)).<sup>109, 110</sup>

Apart from eliminating issues with phase separation, CPEs also offer the opportunity for solution processing from more benign polar solvents, such as water<sup>109, 110</sup> and alcohols,<sup>34, 114</sup> than the typical organic solvents necessary to dissolve and

process CPs. It should, however, be acknowledged that single-component CPE-based LECs so far have failed to match the performance of conventional multi-component LECs, and that a consistent issue has been a slow turn-on, which can be attributed to a low ion mobility within the stiff CP matrix.

### 3.6 Polymerisable electrolytes

On a number of occasions throughout this review, we have in brief mentioned the opportunity of stabilising the *dynamic p-n* junction doping profile by ion immobilisation, and thereby attaining a quick response time and presumably an improved stability of LEC devices. This 'static-junction' (or 'frozen-junction') concept was invented by Gao and coworkers when they stabilised the *in-situ* formed doping profile in a PEO-based active material by lowering the temperature below the  $T_g$  of PEO, *i.e.*, below 200 K, at which the ion mobility in a PEO matrix is effectively zero. A significant number of researchers have tested this concept,<sup>34, 86</sup> but a persistent drawback relates to that LECs (in agreement with other light-emitting technologies) are exposed to relatively significant Joule heating during operation, and that the long-term stability of a frozen static junction thereby in effect is limited.<sup>34, 67, 117</sup>

An interesting alternative strategy to the freeze-out of the ionic mobility constitutes a *chemical* stabilisation, as first demonstrated by Leger *et al.* through the use of polymerisable ion-pair monomers (see Fig. 10(a)).<sup>31</sup> During the initial operation of LECs based on such compounds, free-radical

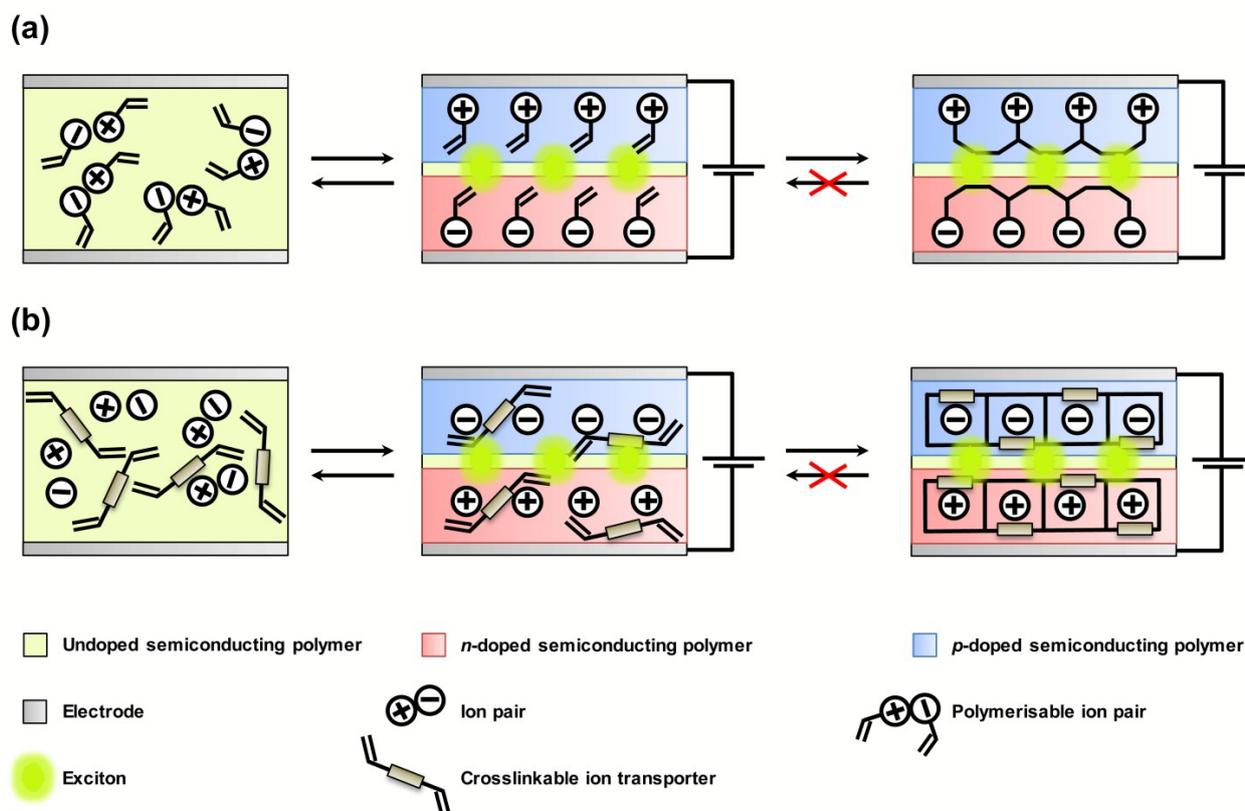


Fig. 10 Schematic illustration of two strategies to attain chemically stabilised LECs, going from (left to right) the pristine device, over the doped device, to the chemically stabilised device under steady-state operation. The chemical stabilisation is attained either from the polymerization of an ion-pair monomer (a) or the crosslinking of the ion transporter (b).

polymerisation of the monomers is believed to take place at sites of electrochemical doping and the polymerised ions are, as a consequence of size and entanglement, effectively immobilised. Although the feasibility of the concept indeed was demonstrated, the performance of the static-junction devices was poor in comparison to dynamic-junction devices. The authors believed that the subpar performance was related to a low mobility of the employed ion-pair monomers,<sup>31</sup> and in a follow-up study they therefore introduced a new group of polymerisable ion-pair monomers with lower melting points and better compatibility with the CP. However, although some improvements were observed, the stability and maximum brightness were still not impressive.<sup>118</sup>

Other strategies for the attainment of improved static-junction LECs by chemical or photochemical means include the employment of crosslinkable ion transporters for a higher initial ion mobility (see Fig. 10(b)),<sup>79, 119, 120</sup> the inclusion of a radical initiator to the active material blend for a more complete crosslinking and a better temporal control of the onset of the polymerisation reaction,<sup>120, 121</sup> or a combination of several of these approaches.<sup>120</sup> Although the concept of static-junction LECs is elegant and their performance gradually has improved over time, it must be acknowledged that the idea of performing a selective free-radical polymerization of (a constituent of) the electrolyte within a CP matrix is highly challenging in the context of the well-established sensitivity of CPs to degradation.<sup>122-124</sup>

#### 4 Conclusion and outlook

The electrolyte plays a crucial role in the function of an LEC, and with a recent improved understanding of the operational mechanism, it has become possible to identify critical electrolyte parameters with regards to, *e.g.*, ion concentration, electrochemical stability, and phase compatibility with the electroluminescent organic semiconductor. Through the consideration of one or several, but not all, of these specifications, it has also been possible to realise LEC devices with distinctly improved performance, albeit not yet on par with that of state-of-the-art OLEDs.

The most commonly utilised electrolyte groups in LECs – alkali metal salts dissolved in ether-based ion transporters and ionic liquids – are imports from neighbouring scientific fields, while polymerisable electrolytes and mixed ion and electron conductors were to some extent explicitly developed to address LEC-specific issues such as a slow turn-on time and phase separation. It must however be admitted that the efforts dedicated to the design and synthesis of a ‘complete’ electrolyte that considers all of the specific requirements of LECs is rather limited, and as a concluding remark we therefore challenge the electrolyte and LEC communities to develop such electrolytes. More specifically, a visionary LEC electrolyte should feature a wide electrochemical stability window that encompasses the *p*- and *n*-type doping potentials of the organic semiconductor, a high ambient ionic mobility, and a good phase compatibility with the semiconductor.

#### Acknowledgements

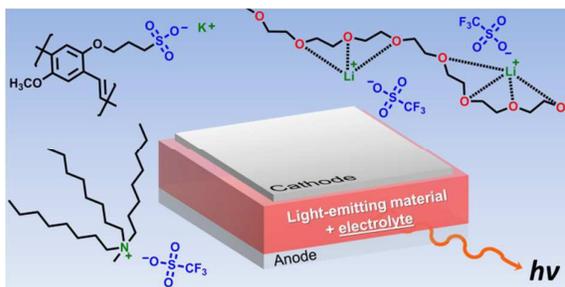
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The role of the electrolyte in light-emitting electrochemical cells is reviewed, with a focus on how it influences key performance metrics.