Charge-Mobility Benchmark Measurements for Natural Photovoltaic

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Abstract

As the business advances, there is an increasing interest for basic, reproducible estimations of the basic material boundaries that influence gadget execution. These are commonly used to streamline measures or to survey the capability of new materials in innovative work programs, or as quality control for material creation. Charge transport in organic semiconductors is critical to good device performance. In OPVs, efficient, balanced charge transport reduces current losses from recombination.

1. Introduction

Natural semiconductors are utilized in the arising natural gadgets industry as the fundamental dynamic materials for func-tional gadgets, for example, natural slight film semiconductors (OTFTs), natural photovoltaics (OPVs) and natural light-transmitting diodes (OLEDs). As the business advances, there is an increasing interest for basic, reproducible estimations of the basic material boundaries that influence gadget execution. These are commonly used to streamline measures or to survey the capability of new materials in innovative work programs, or as quality control for material creation.

Charge transport in organic semiconductors is critical to good device performance. In OPVs, efficient, balanced charge transport reduces current losses from recombina-tion and series resistance losses under high irradiances [1–4]. In OLEDs, good charge transport is important for achieving a combination of high efficiency and high bright-ness [5]. Charge transport in organic semiconductors has been described by models of varying complexity, including device-level and molecular-level models requiring many parameters [6–10]. However, engineers focussed on appli-cations often favour reduction to a simpler description with a single parameter that can be used to benchmark and compare different materials. Typically the preferred parameter is 'mobility' – the mean charge velocity divided by the electric field.

In disordered materials, such as typical organic semi-conductors or amorphous inorganic materials, care needs to be taken with the concept of mobility. Scher and Mon-troll noted in 1975 that *".. .the simple notion of a mobility, field dependent or otherwise, is very limited."* [11] Orders of magnitude variations in mobility values measured on the same material using different techniques are common and widely accepted in the field; though they are not often candidly discussed, and even less often quantified. Never-theless, mobility measurements can be useful for screening applications if properly used. In the context of a small interlaboratory study of mobility measurements on a set of organic semiconductors, this paper is intended to help readers to understand and manage some of the uncertain-ties in mobility measurements. The focus is on mobility measurements applicable to diode structures, such as OLED and OPV devices. The results do not apply to OFETs, which operate in a completely different transport regime [12,13] and have relatively harmonised measurement pro-cedures. We briefly discuss the challenges and advantages of different techniques and focus on the simplest and most versatile method: the space-charge limited current–volt-age (SCLC) technique. We identify the major sources of experimental errors that affect device reproducibility. Strikingly, we demonstrate that different approaches to data analysis are one of the major sources of uncertainty when extracting mobility data from these measurements. To tackle this issue and improve reproducibility of mea-surements, we propose a protocol for data analysis and show that standard deviation can be significantly reduced. In Section 2 of this paper we describe the fabrication of devices used for experimental studies. In Section 3 we briefly compare different methods of measuring mobility in diode structures. In Section 4 we report on the reproduc-ibility of the SCLC technique and propose a protocol for data analysis. In Section 5 we use sensitivity analysis to analyse the sources of variation in SCLC mobility measure-ments. In section 6 we discuss and summarise our conclu-sions. Readers who are familiar with the SCLC technique may wish to skip directly to Section 4, 5, or 6.

2. Device fabrication

Sandwich-type devices were fabricated by spin-coating organic semiconductor films of different thicknesses (from 60 nm to 1100 nm) from toluene solution onto patterned transparent indium tin oxide (ITO) coated glass substrates coated with poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) (Clevios AI4083). These were capped with thermally evaporated top electrodes, defining active device areas of 0.04 cm² overlap between the top electrode and ITO.

For the semiconductor layer, three fluorene-based alternating copolymers were studied: F8BT, TFB and PFB (see supplemental information for chemical structures [14]). Previous studies of similar materials have found hole transport to be relatively poor, and characterised by strong energetic disorder [6,15,16]. They present an interesting challenge for studying charge transport measurements, as mobility is predicted to vary with electric field, charge density and time (under transient conditions), and were chosen to present a "worst-case" scenario. These materials are anecdotally reported to be relatively air stable. The approximate highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies are displayed in Fig. 1. PEDOT:PSS acts as a transparent hole-injection layer (HIL) and electron-blocking layer with a work function of around 5.1–5.3 eV [17]. For some materials, an energetic barrier is expected for hole injection from PEDOT:PSS (i.e. 0.5–0.9 eV barrier for F8BT). Gold was used as a top electrode. The Fermi level of gold (work function 4.5 eV under these conditions [18,19]) is expected to lie within the band gap of all three materials, presenting an energetic barrier to injection of both electrons and holes. A duplicate set of devices was created with a 5 nm interlayer of MoO_3 thermally deposited between the polymer semiconductor layer and the gold top electrode. MoO_3 acts as a HIL with a high work function (between 5.6 eV and 6.8 eV [20]) that is sufficient to inject holes efficiently into most conjugated polymers, including F8BT [16,21].

Devices were fabricated in nitrogen-filled glove boxes. For interlaboratory studies, duplicate sets of devices were fabricated at the same time and transported in vacuum-sealed packages. Devices were stored in nitrogen- or argon-filled gloveboxes and measured in air-tight containers filled with gas from the gloveboxes. During transport and measurement of the devices, monitoring of the quality of the atmosphere was impossible. These conditions are typical of those used for research and development in the field.

3. Mobility measurement techniques

In our initial study, mobility measurements were performed at different laboratories using a range of techniques. These were the steady-state space-charge limited current (SCLC) method and the transient methods: time-of-flight (ToF), dark-injection transient current (DITC) and charge extraction by linearly increasing voltage (CELIV). SCLC was the only technique that was able to extract a mobility measurement on every device. However, as we describe below, this does not necessarily mean that the extracted mobility values were consistent. The transient
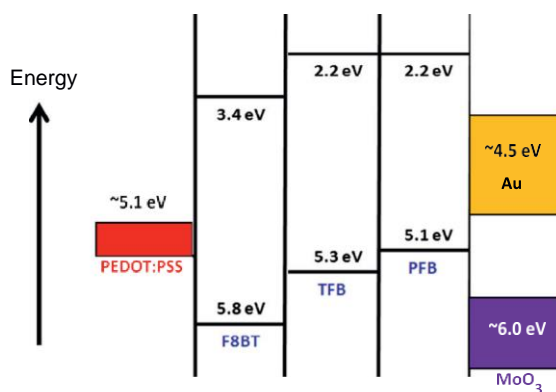

Fig. 1. Approximate energy-level alignment diagram showing the LUMO and HOMO energies of the three organic semiconductors studied and the Fermi levels of three electrode materials. Note that typical uncertainties on these values are ±0.2 eV.

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techniques were found to be less versatile, and only gave results when specific conditions were met.

The mobility values measured by transient techniques (not shown) were higher than the highest SCLC measurements by as much as a factor of 10. This can be explained by charge trapping, or other forms of anomalous dispersion, in which charge carriers undergo relaxation on the timescale of the experiment [22–25]. Such relaxation can occur progressively over a broad range of timescales, leading to a continual decrease of mobility with time over several orders of magnitude [26–28] and the measured mobility can depend on the conditions of the experiment, such as electric field and film thickness [29]. While some reports have successfully combined different transient techniques using multiparameter models to extract detailed information about trap states in materials [6,28,30,31], these approaches are typically too specialised for use in general material screening applications. We briefly describe the reasons for the lack of versatility of the transient techniques: ToF measurements require that photogenerated charge is produced close to one electrode, and that the transit time of carriers is greater than the *RC* constant of the measurement circuit. This prevents measurement of films thinner than ~ 1 lm. Films must also be sufficiently non-conductive [32]. DITC measurements [33] suffer from problems with capacitive effects that create difficulties for measurements on thin films. On thicker films, transient features may be too weak to measure, or can disappear altogether due to charge trapping [34]. CELIV requires films to be sufficiently conductive [32]. In

the study reported here, the intrinsic carrier density plus photocarriers generated by background light were insufficient to produce a measurable signal. Bias light or pulsed excitation can be used, although this introduces additional complexity. Also, the polarity of the measured charge carriers cannot be identified.

We therefore argue that the SCLC technique is most versatile for material benchmarking applications, with the possible exception of some high electron-mobility materials in which electron injection can be problematic [35–37]. It also has the advantages of modest equipment requirements and, being steady state, reproducing conditions relevant to the application in OLED and OPV devices. For this reason, we performed a study to investigate the limitations of using this technique specifically for the purpose of making comparisons between materials, formulations, or processes. Here, accuracy is less important than reproducibility. Accuracy is also difficult to quantify; the reduction of charge transport to a single mobility value is an oversimplification. Thus, we refer to the single value extracted from SCLC measurements as a 'mobility benchmark'.

For SCLC measurements, a hole-only or electron-only diode device structure is required. At least one electrode must efficiently inject the required charge carrier, while the other must block injection of charge carriers of the opposite polarity. When a voltage is applied to the diode, unipolar charge is injected into the semiconductor film, resulting in a build-up of space-charge [38]. Given suffi-

the injecting contact, and the amount of charge inside the device saturates. New charge is injected only to replace charge that is extracted at the opposite electrode. Assuming a uniform charge-carrier mobility, the steady-state current density J_{SCLC} is theoretically a function of the applied voltage V, the film thickness d, the permittivity of the film e, and the steady-state charge-carrier mobility l_{SCLC}:

$$J_{SCLC} = \frac{9}{8} l_{SCLC} e \frac{V^2}{d^3}; \qquad (1)$$

In reality, the mobility commonly varies with electric field. For this reason, a modification to this model developed by Murgatroyd [39] is used, in which the mobility is assumed to take the form:

$$l = l_o \cdot \exp\left(c\sqrt{F}\right); \qquad (2)$$

where l_o is a new parameter representing the mobility in the limit of zero electric field, c is a parameter that describes the strength of the field-dependence effect, and F is the electric field. This general field dependence of mobility can arise from shallow trapping or disorder [22]. It can also hide other effects, such as carrier-density dependent mobilities and deep trapping, which can only be separated by more detailed modelling combined with experiments covering a large parameter space [6,15,16,40,41]. Taking into account that the electric field is not constant throughout the film, Murgatroyd approximated the SCLC current density to:

$$J_{SCLC} = \frac{9}{8} e \frac{V^2}{d^3} l_o \cdot \exp\left(0.89 c \sqrt{\frac{V}{d}}\right); \qquad (3)$$

cient time (greater than the carrier transit time), the space-charge is sufficient to diminish the electric field at

SCLC mobility measurements are typically performed by measuring steady-state current–voltage (I–V) curves and fitting with either of Eqs. (1), or (3) by varying the fit parameters (l_{SCLC} or l_o and c) with other parameters (V, d, AND e) known or assumed. The advantage of Eq. (3) is that it is able to fit a broader range of I–V curves. The disad- vantage is that an additional parameter is required, adding uncertainty and confusing comparisons between materials.

The most important assumptions of the theory are as follows:

- *Charge injection is efficient:* the injecting electrode must be capable of injecting sufficient current into the organic semiconductor film to maintain a current that is bulk-limited rather than interface-limited. This is generally achieved by using an electrode that has a work function aligned to the desired HOMO or LUMO level of the semiconductor and has a low contact resis- tance. As injection limited behaviour can have similar characteristics to space charge limited behaviour, this condition can be difficult to verify experimentally and can lead to false mobility measurements. Poor charge injection becomes a more serious issue in thinner films, where more current is required to sustain SCLC. For any electrode/semiconductor combination there will be a minimum thickness at which SCLC measurements can be successfully made. For many measurements, there will also be a minimum voltage required to achieve SCLC [42].

- *Series resistance does not dominate:* Similar to the above, external series resistances (e.g. from thin-film electrode materials used for contacting) can reduce the voltage dropped across the semiconductor film when the cur- rent is high. This is often identified by the

- current–volt- age curve becoming linear at high voltages. This is particularly an issue where thin films of high mobility materials are to be characterised. There are several strategies for dealing with this problem, including: using four-wire current–voltage measurements, using thicker films to reduce the overall current, and design- ing device geometry to maximise the ratio of conductor width to active area.

- Devices are unipolar: For hole-only devices, the injec- tion of electrons from the collecting electrode must be blocked and *vice versa* for electron-only devices. This can be verified by comparing different electrodes com- binations (see below). Checking for light emission is a common test for bipolar charge transport; emission of visible light under an applied voltage indicates that electron–hole recombination is occurring inside the device, and therefore is unsuitable for SCLC mobility measurements. However, the absence of visible emis- sion does not necessarily guarantee unipolar behaviour.

- *Built-in voltage and* e *are known:* Diode structures usually

  contain built-in voltage V_{BI} due to mismatch between the two electrode work functions and interfaces, even when the electrode materials are nominally the same. V_{BI} is dif- ficult to measure, but can be estimated. If V_{BI} is known, it can be compensated for by applying an offset to the volt- age $V = V_{ext}$—V_{BI}, where V_{ext} is the applied external volt- age. If V_{BI} is unknown, then this introduces additional uncertainty. The relative uncertainty is reduced in thicker films where higher applied voltages are used.

  The value of e is also difficult to measure, though most

  organic semiconductors have dielectric constants in the range $3.0e_o < e < 4.0e_o$, where e_o is the permittivity of free space. Typically a relative dielectric constant of $3.5e_o$ is assumed, as is used in this work.

- *Charge trapping:* Traps are present in organic semicon- ductors as a result of disorder, contamination, defects, or degradation. They have been identified as a particu- lar issue for electron transport in polymers [41,43]. When charge traps are present in a system, a portion of charge carriers will be trapped, while the remainder will be free to move. The 'effective mobility' is an aver- age mobility that includes both free and trapped carri- ers. If the ratio of free carriers to trapped carries is independent of voltage, then the SCLC method applies using the effective mobility. Many models, however, predict that the proportion of free carriers increases with voltage as deep traps become completely filled [30,31,16,40]. This creates a 'trap-filling' region of the *I*−*V* curve in which the current rises exponentially or as a power-law function

of voltage. Eq. (3) will not fit to this region. The field-dependence of mobility in this equation will, however, cope with the effects of shallow traps where the effective barrier to transport is reduced by the application of an electric field.

Doping: Ionised dopants may be present in significant quantities in organic semiconductors. Although they

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do not suffer the effects of coordination defects found in inorganic semiconductors, they are generally thought to be caused by contaminants, and are likely to be mobile. For example, reversible doping by oxygen can create an ionised acceptor population of greater than 0.1% of monomer units in polythiophenes [44]. When doping is of the right polarity (i.e. p-type in hole-only devices or n-type in electron-only devices), the main effect of doping is to increase Ohmic conductivity at low fields. Usually this Ohmic region of the $I–V$ curve is easily ignored. Doping of the wrong type (n-type in hole only devices), the dopants act as deep traps, lead- ing to the trap-filling regime regime above that has a similar effect on $I–V$ curves as an increased built-in volt- age. Some researchers have argued that the SCLC effect is masked by field-dependent ionisation of impurities (the Frenkel effect) [45,46], although this was ruled out on the devices measured in this article by testing the thickness dependence of the current.

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