Dielectric Properties and Conductivity of Iron Oxide-Barium Titanate Composites

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Abstract
Sintered composites of iron oxide plus barium titanate in form of core-shell structures are investigated by impedance spectroscopy. The measurements were performed in the frequency and temperature ranges 20 Hz to 1 MHz and 150 K to 510 K, respectively. The composites exhibit strong low-frequency dispersion of electrical modulus and dielectric permittivity which is caused by different mechanisms of electron transfer at low and high temperatures. A hopping transport process with activation energy of 0.22 eV for exchange between Fe$^{2+}$ and Fe$^{3+}$ was tentatively assigned to reign below room temperature. It gradually changes to a conducting mechanism with activation energy of 0.45 eV above 345 K.

I. INTRODUCTION

Though common materials used for photovoltaics (i.e., the conversion of sunlight into electrical energy) are inorganic, there has been a tremendous effort to develop organic solar cells within the last three decades. The field started by the application of small organic molecules (pigments), and since the development of semiconducting polymers, these materials were incorporated into organic solar cells resulting in remark- able improvements within the past years. The potential of semiconducting organic materials to transport electric current and to absorb light in the ultraviolet (UV)-visible part of the solar spectrum is due to the sp2-hybridization of carbon atoms. For example, in conducting polymers the electron in the pZ-orbital of each sp2-hybridized carbon atom will form π-bonds with neighboring pZ electrons in a linear chain ofsp2- hybridized carbon atoms, which leads then to dimerization (an alternating single and double bond structure, i.e., Peierls distortion). Due to the isomeric effect, these π-electrons are of a delocalized nature, resulting in high electronic polarizability.

An important difference to inorganic solid-state semiconductors lies in the generally poor (orders of magnitudes lower) charge-carrier mobility in these ma- terials, which has a large effect on the design and ef- ficiency of organic semiconductor devices. However, or- ganic semiconductors have relatively strong absorption coefficients (usually >105 cm$^{-1}$), which partly balances low mobilities, giving high absorption in even <100 nm thin devices. Another important difference to crystalline, inorganic semiconductors is the relatively small diffusion length of primary photoexcitations (called excitons) in
these rather amorphous and disordered organic materials.\textsuperscript{9,16–23} These excitons are an important intermediate in the solar energy conversion process, and usually strong electric fields are required to dissociate them into free charge carriers, which are the desired final products for photovoltaic conversion. This is a consequence of exciton binding energies usually exceeding those of inorganic semiconductors.\textsuperscript{24,25} These features of organic semiconducting materials lead generally to devices with very small layer thicknesses of the order\textsuperscript{100} nm.

Most of the organic semiconductors are hole conductors and have an optical band gap around 2 eV, which is considerably higher than that of silicon and thus limits the harvesting of the solar spectrum to a great extent. Nevertheless, the chemical flexibility for modifications on organic semiconductors via chemical synthesis methods as well as the perspective of low cost, large-scale production drives the research in this field in academia and industry.

The organic solar cell development gained momentum in the past years: Conversion efficiencies between 1.5 and 4\% have been achieved for evaporated bilayer devices,\textsuperscript{56–58} bulk heterojunction polymer–fullerene

\begin{figure}
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\includegraphics[width=\textwidth]{figure1.png}
\caption{Illustration of the photoinduced charge transfer (left) with a sketch of the energy level scheme (right). After excitation in the PPV polymer, Conceptually similar to the bulk heterojunction, there is a wide research field of dye sensitized, electrochemical solar cells. The early steps in the development\textsuperscript{74–79} were largely improved by the Graetzel group.\textsuperscript{80} To review this field of electrochemical photovoltaic cells would be beyond the scope of this article, and the interested reader is advised to read the literature in this research area (e.g., Refs. 82–84). However, in recent years, by the introduction of organic hole conductors\textsuperscript{19,71,72,84–89} as replacement for the liquid electrolytes in electrochemical solar cells and by the exchange of the electron conducting acceptor materials in organic heterojunction devices with inorganic nanocrystals,\textsuperscript{73,90–95} electrochemical and organic photovoltaic research directions are gradually merging together.

For practical application, not only the power conversion efficiency but also the lifetime of the photovoltaic device is of importance. The stability of organic solar cells is mainly affected by photo
degradation of the active materials. However, encapsulation techniques as applied in organic light-emitting diodes (LEDs) can provide an efficient sealing against oxidizing agents, but still a high intrinsic photo stability of the organic materials is required.

In the next section, we briefly introduce commonly used materials, followed by a section discussing the main preparation techniques for organic solar cell devices. Thereafter, basic operation principles of photovoltaic light conversion are reviewed, followed by a section presenting the different types of devices. Finally, a section on the control of performance-limiting factors will re-view recent developments, and promising new approaches are discussed as outlook.

II. MATERIALS

Plants use the natural process of photosynthesis to convert sunlight into chemical energy, where the first step in this process is the absorption of light by the chlorophyll molecule. Interestingly, chlorophyll pigments were also directly applied in a single layer solar cell. Besides the absorption of sunlight and (subsequent) creation of photogenerated charge carriers, a second requirement for solar cell materials is the ability to transport these charge carriers. Both properties are commonly found for materials that have an extended delocalized π-electron system. Phthalocyanine is a representative of the type, hole-conducting materials that work as electron donor. The perylene and its derivatives show an n-type, electron-conducting behavior, and they serve as electron acceptor material. Both of these molecules were often incorporated into evaporated solar cells. Because the optical band-gap of most organic materials is around 2 eV, the thermally excited, intrinsic charge carrier concentrations are rather low. Due to disorder and limited overlap of electronic wavefunctions (van der Waals interactions), also the charge carrier mobilities of organic materials are relatively small and hence they can nearly be regarded as insulators. However, there are possibilities to increase the charge carrier concentration, mostly done via molecular or electrochemical doping. Donor type materials show a doping effect when exposed to oxygen or other strong oxidizing agents such as iodine. This doping is achieved by transferring an electron from the ground state S0 of the organic semiconductor to the oxidizing agent, resulting in increased charge carrier concentrations in the hole conductor. As an example forr-type doping, perylene was doped upon exposition to hydrogen. Due to these doping effects, the formerly rather insulating materials possess free charge carriers and bilayer devices can work like classical p–n junctions. However, doping with gases is not very well controllable. A more controlled approach of doping is achieved by the co-evaporation of both materials, matrix and dopant. Among others, the buckminster fullerene C60 and derivatives is a strong electron acceptor. Blended with hole-conducting materials, it does not improve charge transport in the dark, but leads to a large increase in photoconductivity under illumination. This is a result of the photoinduced charge transfer, and hence this process can be viewed as “photodoping”. The chemical structures of some molecular materials are depicted in Fig. 2. In Fig. 3, some commonly used conjugated polymers are shown. Three important representatives of hole-conducting donor type polymers are MDMO-PPV (poly[2-methoxy-5-(3,7-dimethoxycarbonyl)]-1,4-phenylenedine), P3HT (poly[3-hexylthiophene-2,5-diyl] and PFB (poly[9,9’-dioctylfluorene-co-bis-N,N’-(4-butylphenyl)-bis-N,N’-phenyl-1,4-phenylenediamine). They are shown together with electron-conducting acceptor polymers like C80-MEH-PPV (poly-[2-methoxy-5-(2’-ethoxyhexyloxy)]-1,4-(1-cyanovinylene)-phenylene) and F8TB (poly[9,9’-dioctylfluorene-co-benzo thiadiazole] and a soluble derivative of C60, namely PCBM (1-(3-methoxycarbonyl) propyl-1-phenyl[6,6]C61). All of these materials are solution processible due to their
side-chain solubilization, and the polymers show photo- and electroluminescence. 107–109 For the construction of donor–acceptor solar cells, the donor polymers can be either combined with an acceptor polymer or with fullerenes either in planar or diffuse bilayer structures or in blends (compare Sec. IV). To display the fraction of the sunlight, which can contribute to energy conversion in these materials, absorption coefficients of films of some materials are shown in comparison with the air mass (AM) 1.5 standard solar spectrum in Fig. 4. Though the silicon absorption spectrum extends up to 1100 nm, the organic materials use only the blue side of the solar spectrum.

Charge carrier nobilities in films of molecules and conjugated polymers often depend on the nanoscopic or- der, which can be manipulated by the preparation con- ditions. 110–113 For example, a preferential orientation of polymer backbones parallel to the substrate 114, 115 gives rise to an anisotropic charge transport. 112, 113 An over- view on some materials used for organic field-effect tran- sistors (FETs) is reported by Dimitrakopoulos. 15 How- ever, charge transport in FETs is in lateral direction (par- allel to the substrate) contrary to solar cells and most LEDs. For bulk heterojunction solar cells, it was ob- served that the charge transport in such blend structures is a sensitive function of the nanomorphology of the mixture. 116–119

FIG. 3. Several solution processible conjugated polymers and a fullerene derivative used in organic solar cells. Upper row: thep-type hole- conducting donor polymers MDMO-PPV (poly(2-methoxy-5-(3,7-dimethyloctyloxy))-1,4-phenylenevinylene), P3HT (poly(3-hexylthiophene-2,5-diyl) and PFB (poly(9,9′-dioctylfluorene-co-bis-N,N′-(4-butyphenyl)-bis-N,N′-phenyl-1,4-phenylenediamine). Lower row: the electron- conducting acceptor polymers CN-MEH-PPV (poly-[2-methoxy-5-(2’-ethylhexyloxy)-1,4-(1-cyanovinylene)-phenylene) and F8TB (poly(9,9′-dioctylfluorene-benzothiadiazole) and a soluble derivative of C60, PCBM (1-(3-methoxycarbonyl) propyl-1-phenyl[6,6]C61).

FIG. 2. Some organic molecules commonly applied in evaporated organic solar cells: ZnPc (zinc- phthalocyanine), Me-Ptcdi (N,N′-dimethyl- perylene-3,4,9,10-dicarboximide), and the buckminster fullerene C60.

III. PREPARATION TECHNIQUES

The two most common techniques for thin film pro- duction are in a way complementary for the choice of materials. Whereas for evaporation thermal stability is required, materials for solution processing need to be soluble. Small molecules may be thermally more stable but less soluble than polymers, where solubility often is achieved by side-chain solubilization. Polymers will de- compose under excessive heat and have a too large molar mass for evaporation. Hence for small molecules, evapo- ration is the best choice, whereas semiconducting poly- mers are mainly processed from solution. However, less soluble molecules like C60 may become soluble when modified by attaching solubilizing groups (e.g., PCBM) and short polymers or oligomers may also be evaporated. 67, 120

A. Evaporation

To grow films by thermal evaporation, usually a vacuum of <10–5mbar is applied. Thus the mean free path of the evaporated molecule is longer than the dis- tance between the evaporation source and the sample holder. In addition, contaminants like oxygen and water are reduced and can be eliminated.
further by ultra high vacuum (<10−9mbar) or evaporation inside of a glove box with inert atmosphere. To create interpenetrating do- nor-acceptor networks or to achieve molecular doping, co-evaporation techniques can be applied.37,67,69,102,121

B. Wet processing

Common to all wet processing techniques is the solv- ing of organic materials in an appropriate solvent like water or any other polar or nonpolar organic solvent. A special case is the solution processing of a soluble mono- mer coupled with a polymerization reaction during (e.g., electrochemical polymerization) or after (e.g., via heat treatment, UV curing, and so forth) the film forming process (precursor route). This has the advantage that after preparation, the resulting polymers are insoluble and another film can be deposited from solution on top of them. If polymers or polymer/polymer or polymer/ molecule blends are directly processed from solution, several common techniques are applied: (i) spin coating, (ii) doctor blading, (iii) screen-printing, (iv) inkjet print- ing, and many more. For example, screen-printing was applied to a MDMO-PPV:PCBM blend (Fig. 5).122This exploitation of existing printing techniques assures an easy upscaling of the production and low energy con- sumption during production of solar cells, which is important for the energy amortization (energy delivered by a solar cell during its lifetime as compared to the energy needed to produce the solar cell itself).

IV. BASIC WORKING PRINCIPLES

The process of converting light into electric current in an organic photovoltaic cell is accomplished by four con- secutive steps: (i) Absorption of a photon leading to the formation of an excited state, the electron-hole pair (ex- citon). (ii) Exciton diffusion to a region, where (iii) the charge separation occurs. (iv) Finally the charge trans- port to the anode (holes) and cathode (electrons), to sup- ply a direct current for the consumer load.

The potential energy stored within one pair of sepa- rated positive and negative charges is equivalent to the difference in their respective quasi-Fermi levels, or in other words it corresponds to the difference in the elec- trochemical potentials.25The larger the quasi-Fermi level splitting remains during charge transport through the in- terfaces at the contacts, the larger will be the photovolt- age. Though for ideal (ohmic) contacts no loss is ex- pected, energy level offsets or band bending at non-ideal contacts (that undergo energy-level-alignments due to Fermi-level differences) can lead to a decrease in the photovoltage.

The electric current that a photovoltaic solar cell de- livers corresponds to the number of created charges that are collected at the electrodes. This number depends on the fraction of photons absorbed (abs), the fraction of electron-hole pairs that are dissociated (diss), and finally

FIG. 4. Absorption coefficients of films of commonly used materials are depicted in comparison with the standard AM 1.5 terrestrial solar spectrum. The overlap is generally small.

the fraction of (separated) charges that reach the electrodes (out) determining the overall photocurrent efficiency (η).

\[ \eta = \frac{\text{absorption}}{\text{dissociation}} \]

The fraction of absorbed photons is a function of the absorption spectrum, the absorption coefficient, the absorbing layer thickness, and of internal multiple reflections at, for example, metallic electrodes. The fraction of dissociated electron-hole pairs on the other hand is determined by whether they diffuse into a region where charge separation occurs and on the charge separation probability there.

To reach the electrodes, the charge carriers need a net driving force, which generally results from a gradient in the electrochemical potentials of electrons and holes. Two forces contribute to this: internal electric fields and concentration gradients of the respective charge carrier species. The first leads to a field induced drift and the other to a diffusion current. Though a detailed analysis requires the knowledge of charge carrier distributions over film depth, thin film devices (<100 nm) are mostly field drift dominated, whereas thick devices, having effective screening of the electrical fields inside the bulk, are more dominated by the diffusion of charge carriers in concentration gradients at the selective contacts.

To understand the rectifying behavior of an intrinsic (nondoped) semiconductor device in the dark, the MIM (metal-insulator-metal) model is useful. In Fig. 6, a semiconductor, sandwiched between two metal electrodes with different work functions is depicted for several situations. The metals are represented by their Fermi levels, whereas for the semiconductor the valence and conduction bands, corresponding to the molecular LUMO (lowest unoccupied molecular orbital) and the HOMO (highest occupied molecular orbital) levels, are shown. In Fig. 6(a), there is no voltage applied (i.e., short-circuit conditions). Hence, there is no net current flowing in the dark, and the built-in electric field resulting from the difference in the metals’ work functions is evenly distributed throughout the device. Under illumination, separated charge carriers can drift in this electric field to
the respective contacts: the electrons move to the lower work function metal and the holes to the opposite. The device then works as a solar cell. In Fig 6(b), the situation is shown for open circuit conditions, also known as “flat band condition.” The applied voltage is called the open circuit voltage $V_{OC}$, which corresponds in this case to the difference in the metals’ work functions and balances the built-in field. As there is no net driving force for the charge carriers, the current is zero. In Fig. 6(c) the situation is shown for an applied reverse bias and only a very small injected dark current $j_0$ can flow. Under illumination, the generated charge carriers drift under strong electric fields to the respective electrodes and the diode works as a photodetector. If a forward bias larger than the open circuit voltage is applied [Fig. 6(d)], the contacts can efficiently inject charges into the semiconductor. If these can recombine radiatively,

FIG. 6. Metal-insulator-metal (MIM) picture of organic diode device function. (a) Closed circuit condition: under illumination photogenerated charges drift toward the contacts. (b) Flat band or open circuit condition: the current becomes zero. (c) Reversed bias: photogenerated charges drift in strong electric fields, the diode operates as a photodetector. (d) Forward bias larger than $V_{OC}$: the injection increases and the diode opens up.

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