Final Technical Report for the Energy Frontier Research Center
Understanding Charge Separation and Transfer at Interfaces in Energy Materials (EFRC:CST)
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Our EFRC, *Understanding Charge Separation and Transfer in Energy Materials* (referred to herein as "the CST"), was founded with the vision of creating a broadly collaborative and synergistic program that would lead to major breakthroughs in the molecular-level understanding of the critical interfacial charge separation and charge transfer (CST) processes that underpin the function of candidate materials for organic photovoltaic (OPV) and electrical-energy-storage (EES) applications. Research in these energy contexts shares an imposing challenge: *How can we understand charge separation and transfer mechanisms in the presence of immense materials complexity that spans multiple length scales?* To address this challenge, our ~50-member Center has undertaken a total of 28 coordinated research projects aimed at unraveling the CST mechanisms that occur at interfaces in these nanostructured materials. By design, these projects emphasized selected model OPV and EES interfaces, accessible to concurrent computational and experimental approaches, in order to correlate interfacial structure and CST processes. This rigorous multi-year study of CST interfaces has greatly illuminated our understanding of early-timescale processes (e.g., exciton generation and dissociation dynamics at OPV heterojunctions;[1] control of Li^+-ion charging kinetics by surface chemistry[2]) occurring in the immediate vicinity of interfaces.

Program outcomes included training of 72 graduate student and postdoctoral energy researchers at 5 institutions and spanning 7 academic disciplines in science and engineering; publication of 94 peer-reviewed journal articles (3 more are in press as of this writing); and dissemination of research outcomes via 340 conference, poster and other presentations.

A. Major Scientific Outcomes:

A summary of major scientific outcomes from this work is presented below. Notably, we have included both research outcomes and descriptions of key techniques, tools and instrumentation capabilities that we developed in order to achieve these outcomes. More details about these EFRC-enabled capabilities can be found in the references cited.

1. Elucidating Morphology in Polythiophene Aggregates via Spectral Properties: We have implemented a hierarchical strategy for understanding the critical aspect of OPV material morphology, the manner in which the molecular components pack and hence communicate electronically. The fundamental problem in developing a structural description of morphology lies in the heterogeneity of the material and the lack of specific probes of molecular geometry. We have integrated synthesis, spectroscopy and computational modeling to address these challenges. We have shown clearly how the density of side chains influences the conformational distributions of single polymers.[3] We have shown that the characteristic red shift in the absorption spectrum for polymer aggregates cannot arise from single chain or even two interacting polymers. Instead, this key observable requires a larger cooperative unit to induce a reduction in torsional distortions.[4] By combining creative synthesis with spectroscopic analysis, we have developed a model nanoscale aggregate OPV system that has opened up a unique window for discovery of the underlying structural features of aggregates. The aggregate is comprised of individual triblock polymers with two moderate sized conjugated polymer segments (~100 monomers, currently poly(3-hexylthiophene) (P3HT)) connected to each other through a comparable flexible linking polymer (~200 units, currently poly(*tert*-butyl acrylate (PtBA)). By changing solvent conditions, this triblock can reversibly self-assemble into self-terminating, small aggregates of ~5 units. These units are found to have absorption spectra nearly identical to a neat film of P3HT.[5] Very recent time-resolved fluorescence spectroscopy of these aggregates has shown that, in contrast to films,[6] the aggregates show a distribution of electronic behaviors, indicating that these capture a variety of structural environments. This system has the enormous advantage that the excitation emission can report on the structure, rather than simply reporting on low energy sites as in films, so that we learn the excitonic heterogeneity with structure. At the same time, the system is accessible to a multiscale simulation strategy, in which solvent is treated implicitly, so that the structure-spectra connection is accessible.[7] Spectroscopic and spatial isolation in the tri-block model provides the opportunity to isolate the relationship between morphology and the nature of the exciton, and it allows us to unravel the dynamic heterogeneity that governs exciton behavior in P3HT thin films.

2. Describing Exciton Dynamics in OPV Systems: We have fully developed a unique simulation capability for describing the non-equilibrium evolution of the electronic dynamics of excited states of large conjugated organic systems.[1] Unlike sequential approaches using molecular mechanics (MM) modeling followed by electronic structure methods for those geometries, it provides a direct description of the *coupled* electronic and nuclear response essential to energy migration and electronic dynamics, and direct access to transient spectroscopies.[1] We have shown, by direct simulation of the electronic and nuclear dynamics, that the rate of exciton dissociation at an interface between P3HT (modeled by one or two oligomers) and fullerene has a non-trivial and non-classical dependence on local fields. In particular, the relative energy of charge transfer (CT) states varies with field and excitonic states are essentially unaffected. The rate of transition from the initially created exciton state to a charge separated state is not a monotonic function of field, as illustrated for a sexithiophene-C_{60} dyad or triad. For a stacked pair of sexithiophenes on C_{60}, the rate has two maxima, where energy gaps are most favorable for relaxation to CT states. Only one of these corresponds to the direction favored by classical electrostatics for electron-hole separation. Hence, conventional speculation on the role of intrinsic fields in materials on charge separation efficiency is not well founded.

3. Probing Recombination Mechanisms in Photovoltaics via New Imaging Geometries: It is becoming increasingly clear that the key factor that currently limits efficiencies in OPV materials is not the generation of charges but rather their recombination. However, the mechanisms of recombination are largely unknown, in part because recombination is a process that involves structural morphology across a wide range of distance scales. Recombination can occur directly after charge separation in so-called geminate recombination, or by bimolecular encounter between charges migrating through the device in a so-called Langevin process. On longer time scales, most polymer systems exhibit such Langevin recombination, especially when trap states are included. However, some materials have demonstrated distinctly "non-Langevin" recombination dynamics, with bimolecular losses far smaller than expected. These materials have exceptional potential to allow for thicker films with far more efficient light collection and power conversion. A lateral OPV (LOPV) device developed within our EFRC has allowed us to model electron and hole distributions in bulk heterojunction materials,[8–10] and to conduct mesoscale imaging studies of photocurrent generation and of local charge distributions. Recombination work has focused on the use of lateral OPVs (LOPVs) that allow for direct access to the material between the electrodes.[10–14] While the distances between the electrodes in these model devices are significantly larger than what is found in a typical vertical OPV device, the applied fields and current characteristics are similar.[12,13,11] Theoretical models predict the existence of regions of space charge limited (SCL) current near each electrode with a "recombination zone" in the middle of the device.[11,12] Our work on photocurrent imaging of a Langevin OPV system (PSBTBT:PCBM) has shown that both the SCL regions extend for lengths around 1 micron with a large recombination zone in the middle of the device.[10,14] In contrast, images of devices made with the non-Langevin polymer KP115 (Fig. 1) demonstrate that photocurrent is generated throughout the entire 20 μm region between the electrodes. This work has allowed us to construct a more comprehensive picture of the

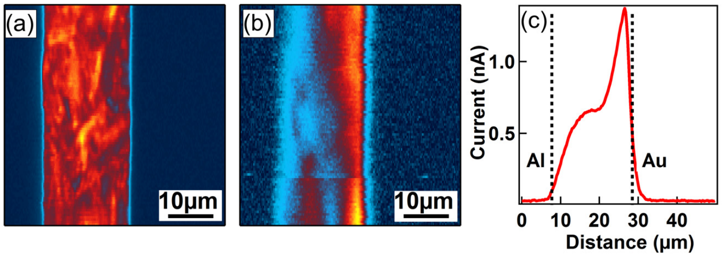

Fig. 1: Fluorescence microscopy and photocurrent image of a LOPV with KP115/$PC_{61}BM$. (a) Fluorescence image (b) Photocurrent image. (c) Average line profile of photocurrent images.

fate of charges in bulk heterojunction materials.

4. Examining the Influence of Surface Chemistry and Alloying on CST Mechanisms in Battery Materials: Our CST efforts in EES have been tightly focused on systematic investigation using integrated experiments and theory of ion-coupled electron transfer processes in model Li-ion battery electrode/electrolyte systems to understand how structure and morphology influence solid state redox reactions. Several reports have noted that surface modification of active materials can reduce the formation of surface impurity phases and facilitate the formation of solid solutions (homogeneous phases) that enhance charge transfer in Li-ion battery materials. We have investigated the roles of solid-state structure,[15–17] electronic properties,[18] and materials chemistry[2] on both the material thermodynamics[17,18] and the rates of ion passage in surface-modified materials.[2,19] The rates and cycling behavior evident in experimental electrochemical studies have been understood in terms of ion binding sites and energetic barriers to transport. We developed *in situ* electrochemical Raman spectroscopy for study of cathode materials to obtain a molecular-level understanding of how different sized and shaped materials behave toward lithium ion coupled electron transfer processes,[16,20] and simultaneously developed theory and simulation of the *in situ* Raman data to determine the nature of Li$^+$ binding and transition metal-oxide and phospho-olivine interactions.[17,19,21] We demonstrated for first time that *in situ* electrochemical Raman can detect the PO$_4^{3-}$ distortion associated with Li$^+$ insertion, which makes it a suitable probe for the study of surface stability and phase changes in cathode materials. Furthermore, we have learned through calculations of the various components of diffusion, including in the bulk, on the surface, in strained materials, and in the presence of defects, that slow surface diffusion and anti-site defects can be possible rate limiting steps owing to the 1-D nature of Li$^+$-diffusion.[16] Bulk diffusion of Li$^+$ along the 1D channels into the material is found to be rapid. Along the surface, however, diffusion is slow because of the corrugated nature of the oxide surface between channels (Fig. 2A). Anti-site defects were also considered; in FePO4, anti-site Fe2+ defects block the channels for Li+ diffusion because of a strong binding energy between two. When a second Li+ is present, (Fig. 2B) a concerted event makes diffusion around the defect facile, which has not been considered before in the behavior of this material. Finally, the functionalization of graphene for coupling to OPV or to EES materials,[22] and our recently demonstrated ability to map the distribution of that functionalization using our EFRC low temperature scanning tunneling microscopy (STM) capabilities,[23] places us in a position to understand how to design graphene chemistry to make it an effective material.

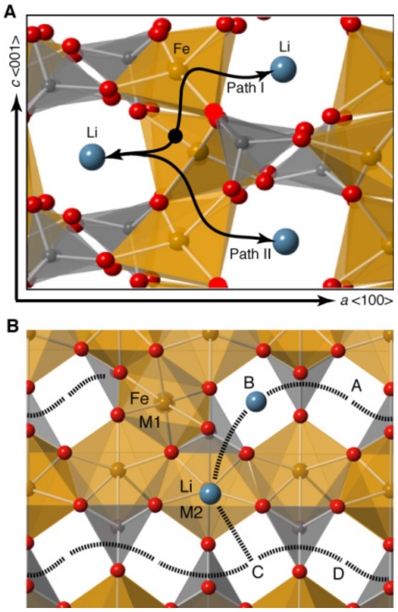

Fig. 2. (A) Rate limiting diffusion is found on the surface of LiFePO$_4$; (B) an exchange mechanism is shown to allow facile diffusion past anti-site defects.

5. Observing Charge Transfer Dynamics in EES Nanostructures in Real Time: Groundbreaking *in situ* transmission electron microscopy (TEM) measurements of the lithiation/delithiation of nanoscale Si or Ge modified with Sn have been carried out, providing the first detailed observation of the spatial distribution of such chemical change and of the transformation of silicon morphology.[24–26] Time-resolved TEM studies comparing Si and Ge nanowires without any Sn and those with significant amounts of Sn have shown that Li diffusion is greatly enhanced by the incorporation of Sn.[25] In addition, reversible nanopore formation was observed in Si nanowires that had high Sn content (8-10 at%); this is the first *in-situ* observation of nanopore formation in Si, and appears to be related to the relatively fast lithiation and delithiation rates of these nanowires (due to Sn incorporation). These direct observations of the morphological changes in Si and Ge nanowires undergoing lithiation and delithiation have provided new insight about what the fundamental limitations might be for Si and Ge anodes in lithium ion batteries and how to overcome them. A separate series of our studies focused on the poorly understood solid-electrolyte interphase (SEI) that initially forms between an electrode and electrolyte and has been shown to be capable of stabilizing or destroying a battery's functionality. Part of the reason that the SEI has been historically difficult to study is that its formation and composition are extremely sensitive to atmospheric air and moisture. We thus developed *in situ* spectroscopic ellipsometry and spectroelectrochemical FTIR for studying polymerized SEI species formed from propylene carbonate (PC) and ethylene carbonate/diethyl carbonate (EC/DEC) electrolyte mixtures at Si and graphite anodes.[27,28] The SEI structures formed at Si surfaces were chemically distinct from those formed at carbon electrodes.[29] This formation mechanism has been a topic of debate in the literature for 20 years and has importance in, among other areas, full cell modeling of batteries for cycle and aging estimates.

B. Additional Technologies and Techniques Developed:

In addition to those described above in Section A, other technologies, methods, and capabilities that we have developed since the program's inception are highlighted briefly below:

- Dynamical excited state simulation of large systems. A newly developed mixed quantum-classical simulation code that has the unique capacity to simulate molecular nuclear and electronic dynamics, including excited state evolution in relatively large, disordered, and thermal samples of conjugated organic molecular materials. This method allows the mechanisms of excitonic relaxation and exciton dissociation to be studied a priori, without presumption of a mechanistic model.

- FTIR Spectroscopy Cell for Thin Film Materials. A new sample holder for thin film IR spectroscopy measurements has been designed to study crystallinity in thin organic films and the interactions between organic thin films and surfaces.

- FTIR Spectroscopy. *In situ* electrochemical FTIR spectroscopy is implemented for the study of Li-ion insertion/extraction processes at electrode interfaces in contact with nonaqueous electrolytes. This capability allows for vibrational spectroscopy to be conducted at various stages of applied potential and time, and *in situ* with millisecond time resolution (i.e. step-scan FTIR configuration).

- Reduced Oxidation (ROx) Interface. An innovative transfer capsule has been designed to never expose air sensitive samples to conditions of higher water and oxygen content than those in the glove box. This capability has the important advantages in that 1) the sealed transfer capsule is attached directly to a pumping chamber and purged thoroughly with nitrogen and pumped to millitorr pressures, *before* transfer capsule is opened; and 2) uses no roughing pump, only a turbo pump, to limit contamination with pumping oils, water and oxygen. The interface is a general tool that can be utilized to study any air sensitive materials, and at present, two such interfaces have been developed, one for XPS analysis and the other for ToF-SIMS analysis.

- Scanning Confocal Photocurrent Microscopy (SCPM). Scanning Confocal Photocurrent Microscopy (SCPM) has been developed and implemented for imaging and analysis of lateral organic photovoltaics to observe space charge regions and mobilities. This technique utilizes confocal microscopy tools as well as steady state current vs. voltage measurements on high aspect ratio nano-fabricated structures in order to probe the material properties between the electrodes. This is the only method to simultaneously measure mobilities of electrons and holes in bulk heterojunctions while locally probing charge recombination and separation.

- Solid State Nudged Elastic Band (SSNEB). A new computational method for determining reaction pathways for solid-solid phase transitions involving both atomic motion and changes in the crystal lattice has been developed. This method allows for the determination of energy barriers for which the reaction mechanisms can be coupled to changes in the crystal lattice, such as Li intercalation.

- Spectroelectrochemical Diffraction Microscopy. High resolution *in situ* spectroelectrochemical diffraction microscopy is employed for the study of volume expansion/contraction during the lithiation/delithiation processes. This capability provides insight into understanding the lithium reaction induced volume change and capacity fading on cycling of Si-based anodes in Li-ion batteries and could be applied generally to study the mechanical changes associated with electrochemical charging of materials.

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