

Recent Advances and Opportunities for Organic Mixed Ionic-electronic Conductors

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Organic mixed ionic-electronic conductors (OMIECs) are soft materials, often polymers, that can conduct both ions and electrons. A striking feature of OMIECs is their ability that enables electronic charge transport along π -conjugated backbones, while supporting ionic transport through bulk. This makes OMIECs ascendant with respect to emerging applications¹, including batteries/supercapacitors², chemical sensors³, neuromorphic molecules⁴, light-emitting electrochemical cells (LEECs)⁵ and in electromechanical actuators for soft robotics⁶. Particularly, OMIECs' implementation in organic electrochemical transistor (OECT) has received much attention due to enhanced biosensing, neuromorphic function, and specialized circuits⁷. For example, it has been reported that the enhanced sensing ability of OMIECs based OECT has surpassed inorganic transistors based on non-mixed conductors⁸. As an OECT channel, OMIECs should exhibit efficient electronic transport and facile ion injection for the purpose of sustaining high capacity. As OMIECs are usually composed of conjugated polymers and electrolytes, design and modulation rules for those two adjacent material classes have been leveraged in recent advances of OMIECs. Ionic-electronic interactions, however, play a very important role in modulating ionic transport and electronic transport of OMIECs.

There are 3 processes involved in OMIECs: ionic transport, electronic transport, and ionic-electronic coupling. The ability to conduct ions sets OMIECs apart from other conjugated semiconductors, of which the mechanisms are shown in Figure 1. The electronic transport occurs in OMIECs due to the presence of delocalized π -orbitals along conjugated backbone, and the strong π - π overlap between molecules. Structural disorder limits the electronic charge carrier mobility and electrical conductivity, leading to low charge transport performance. In OMIECs, however, the charge balance requires the existence of excess ionic charge for the presence of electronic charge, which is commonly referred to as doping. The dopant concentration and

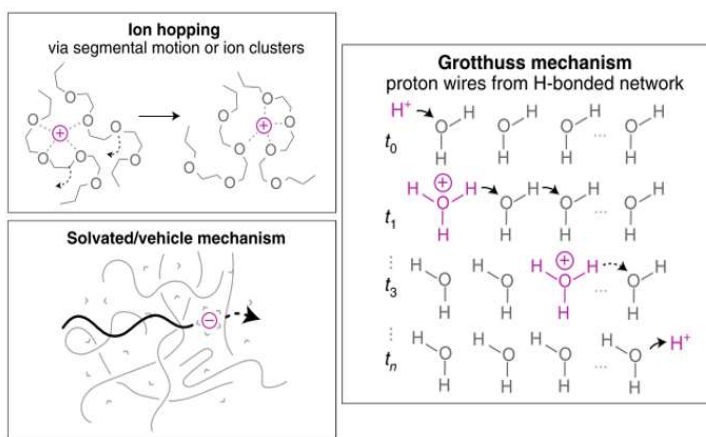


Figure 1. Three different ionic transport mechanisms⁹.

electronic charge carrier density can sensitively affect the electronic carrier mobility as shown in Figure 2. The initial decrease of mobility is due to the Coulombic trapping of ions on carriers. Activation energy of charge hopping decreases with increasing doping level, resulting a steep increase in the carrier mobility. The coupling between electrons and ions can exist homogeneously throughout the OMIEC, or at the interface between microphases separated regions of conjugated polymers and electrolytes depending on the chemistry of an OMIEC⁹. As a result, one cannot consider ionic and electronic transport are independent and must take ionic-electronic coupling into account when achievement of fundamental and applied aims of OMIECs is desired.

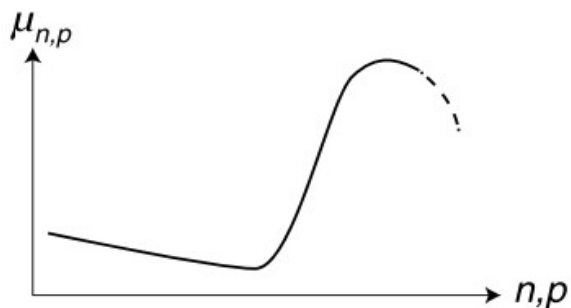


Figure 2. The dependence of mobility on charge carrier density⁹

From a synthetic perspective, materials explicitly designed for OMIECs are required in order to get rapid progress in this emerging subfield of polymer-based electronic devices. Currently the OMIECs materials are synthesized in a way that combines known ion-conducting and charge-conducting components. Typically polyelectrolytes or polymer electrolytes are responsible for ionic transport whereas conjugated polymers are incorporated for charge transport. Those incorporated chemical moieties are usually well-studied in adjacent fields of organic electronics and have shown impressive device performance in some applications. However, due to the considerable ionic-electronic coupling in OMIECs, there is a pressing need of molecular design strategy which addresses the interaction between ions and charge carriers.



Figure 3. Schematic diagram of three central process in OMIECs. The first process (left) is doping and dedoping; second (center) is the morphology changes upon ion penetration; last (right) is the ion-coupled electron transport¹³.

Other than the chemistry, morphology of OMIECs polymers is also critical to determining the ionic-electronic coupling and overall performance. As OMIECs can swell and undergo significant morphological changes upon electrolyte absorption, the electronic transport can be sensitively affected as it is extremely susceptible to structural changes in conjugated polymer phase as shown in Figure 3. To date, the detailed characterization of morphological rearrangement during device operation upon electrolyte absorption is still severely lacking. One would expect the ionic transport would be favored by amorphous morphology whereas electronic transport benefits from crystalline domains, thus a balance in morphology need to be reached for optimal conditions. Several studies, however, have shown this trade-off can be circumvented through synthetic strategies^{10,11}. On the other hand, strategy including using high crystalline morphology coupled with sufficient porosity has also been applied¹². To characterize the morphological changes during operation, computation and theory should be applied in conjunction with experimental techniques.

There are several important questions need to be addressed in order to push the bounds of this field. First, explicit molecular design for OMIECs need to be developed. Second, real-time characterization plays a central role to reveal the morphological changes during processing and operation. Third, the knowledge gap between ultimate device performance and fundamental understanding at molecular level need to be filled.

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