

# Local Ordering for Decoupling Bonding of Mobile Ions and Polymer Matrixes by Zwitterionic Solid Polymer Electrolytes

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**Zwitterionic solid polymeric electrolytes that self-assemble into superionically conductive domains exhibit excellent Li<sup>+</sup> transport properties.**

Solid polymeric electrolytes (SPEs) suffer from low ionic conductivity. For a long time, researchers have been trying to construct SPEs with a low glass transition temperature ( $T_g$ ). Ion motion is influenced mainly by segmental relaxation so that the amorphous domains can significantly enhance the lithium-ion conductivity. Recently, a new ion transport mechanism was proposed. In this issue of *ACS Central Science*, Segalman and co-workers have achieved a breakthrough by designing polymeric zwitterionic SPEs (PZIL) that self-assemble into superionically conductive domains.<sup>1</sup> These locally ordered domains can decouple bonding of mobile ions and polymer matrixes, and enable high selectivity for lithium, which contributes to excellent lithium conductivity (1.6 mS/cm) and a high lithium transference number ( $t^+ \approx 0.6$ –0.8).

SSEs are attracting increasing interest for energy storage and electric vehicles. Replacement of liquid electrolytes with SSEs will not only improve the stability of electrode/electrolyte interfaces and enable long-cycle lives, but they also make batteries safer due to the high thermal stability of SSEs. Thus, all-solid-state batteries are supposed to achieve a higher energy density, longer cycling, and better safety compared to commercial Li-ion batteries with liquid electrolytes.<sup>2</sup> SPEs are promising SSEs due to their stability, flexibility, and processability; however, one of their main drawbacks is their low room-temperature ionic conductivity and transference number.

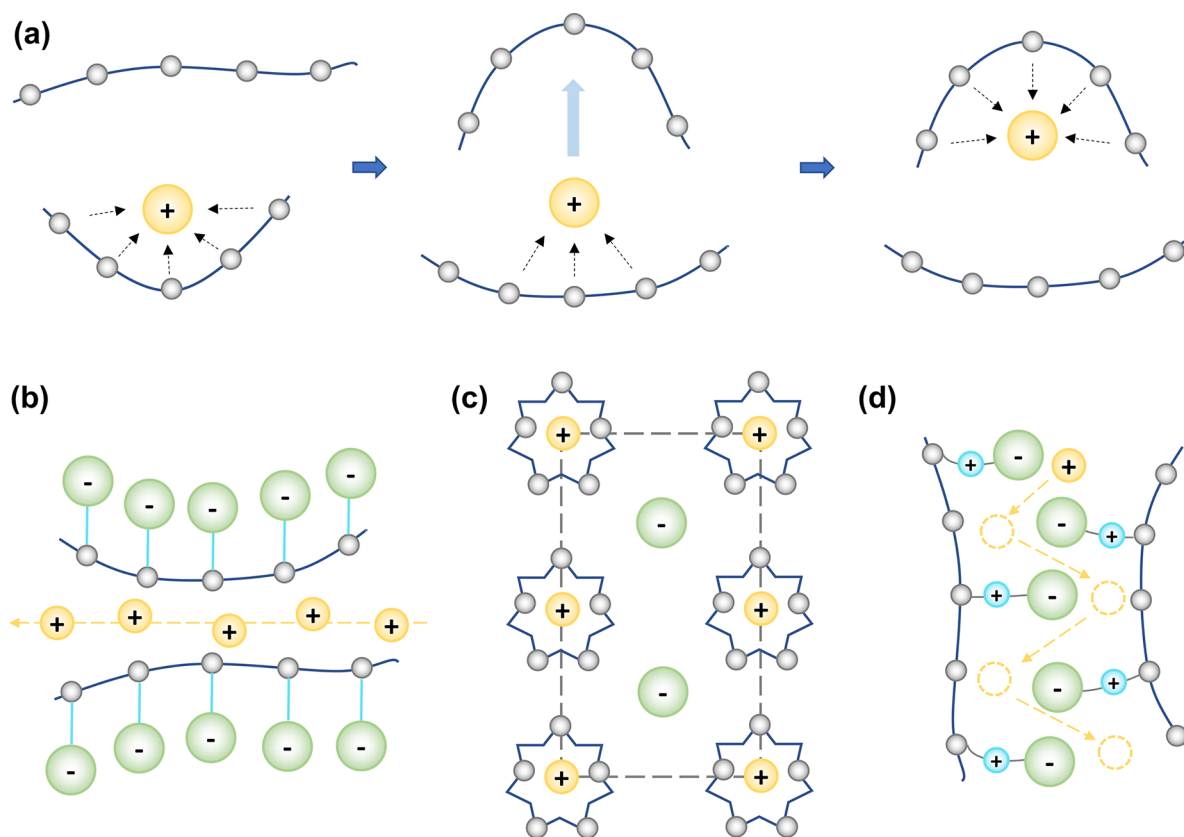
Ionic transport in an SPE was first discovered in poly(ethylene oxide) (PEO) in 1973.<sup>3</sup> In 1983, Armand proposed that only the amorphous domains of SPEs show

an appreciable Li-ion mobility.<sup>4</sup> Druger et al. developed a dynamic bond percolation (DBP) model to describe ion transport in polymer electrolytes.<sup>5</sup> This model characterized the ionic motion in terms of jumps between neighboring positions. Besides, the motion of the Li<sup>+</sup> species between complexation sites is assisted by the segmental motion of the SPE matrix (as **Figure 1a** shows). Thus, the amorphous phase above  $T_g$  with a dynamic, disordered environment facilitates ion transport. In 1984, Bannister et al. proposed a single Li-ion conducting SPE, in which the anionic units were expected to be virtually immobile.<sup>6</sup> With most anions chemically bonded as shown in **Figure 1b**, a higher transference number  $t^+$  will be achieved, and charge flow is mainly contributed by Li<sup>+</sup>, which alleviates the concentration polarization in SPEs.

Segalman and co-workers have achieved a breakthrough by designing polymeric zwitterionic SPEs (PZIL) that self-assemble into superionically conductive domains. These locally ordered domains can decouple bonding of mobile ions and polymer matrixes, and enable high selectivity for lithium, which contributes to excellent lithium conductivity (1.6 mS/cm) and a high lithium transference number ( $t^+ \approx 0.6$ –0.8).

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**Figure 1.** Ion transport mechanism in SPEs. (a) Ion transport in the amorphous phase with segmental motion. (b) Ion transport in a single Li-ion conducting SPE with anions chemically bonded. (c) Ion transport in crystalline polymer electrolytes with a partial occupancy of sites by potentially mobile ions. (d) Ion transport in locally ordered domains of the zwitterionic SPE proposed by Segalman and co-workers.<sup>1</sup>

In 2001, Tunstall's group discovered that ionic conductivity in the crystalline phase of SPE can be greater than that of the equivalent amorphous material above  $T_g$ .<sup>7</sup> Crystalline polymer electrolytes with suitable structures and with a partial occupancy of sites by potentially mobile ions enable selectivity for  $\text{Li}^+$  ion transport (cation transport number  $t^+ = 1$ ) (see Figure 1c). In 2003, Angell and co-workers explored a new rubbery polymer-in-salt type electrolyte with  $\text{LiClO}_4$  at a high content, exhibiting a high ionic conductivity.<sup>8</sup> This is ascribed to the fact that lithium cation motion is highly decoupled from the structural relaxation. The crystallization of the salt at a high content favors  $\text{Li}^+$  transport.

The above research studies mainly discuss the effect of the amorphous phase or crystalline phase within the whole electrolyte on the ionic transport property. The work by Segalman and co-workers has paid attention to the influence of locally ordered domains in ion transport. It inspires a new material design strategy for SPEs with high ionic conductivity by decoupling lithium transport from the fluidity of the matrix. With both locally ordered (as shown in Figure 1d) and amorphous domains working together, this zwitterionic SPE has a comparable conductivity but a much higher  $\text{Li}^+$  selectivity, in comparison to the best conventional SPEs.

The conduction behavior of PZIL resembles a locally ordered inorganic solid ionic conductor.

With both locally ordered (as shown in Figure 1d) and amorphous domains working together, this zwitterionic SPE has a comparable conductivity but a much higher  $\text{Li}^+$  selectivity, in comparison to the best conventional SPEs. The conduction behavior of PZIL resembles a locally ordered inorganic solid ionic conductor.

In spite of the novelty of this finding, some uncertainties are worth investigating further. For SPEs, either amorphous, ordering, or locally ordering phases can show enhanced ionic conductivity in different systems. For comparison, a high crystalline phase, such as glass, glass-ceramic, etc., can show superior ionic conductivity in different inorganic electrolytes. How can we understand the unique behavior of PZIL in different kinds of SPEs? Are zwitterionic molecules a key requirement in forming such a locally ordered

structure? In addition, it is known that ion transport can be enhanced at the interfacial region through a space charge effect. A famous example is the soggy-sand type electrolyte.<sup>9</sup> What could be the continuous ionic transport paths in this report where locally ordered and amorphous domains coexist? Taking the electrochemical stability, mechanical stability, thermal stability, and cost into consideration, how can we optimize this system further for practical applications? A deep and comprehensive understanding and exploration are required for future commercial applications.

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##### Notes

The authors declare no competing financial interest.

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