

Solid Ionic Conductors in High Energy Density Batteries

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In recent years, there has been much interest in the fabrication of high energy density batteries based on the alkali metal intercalation of the layered metal chalcogenide compounds, MX_2 and MPX_3 (Figure 1). These processes are well suited for this use because of the high quantity of energy available, and the ease of reversibility [1]. Although both compound types have similar structures and formulas, the intercalation chemistry has been shown to be quite different in the two. Some of the intercalated MX_2 compounds have been shown to be electrical semiconductors as well as ionic conductors [2]. During intercalation, the lithium donates its electron to the MS_2 conduction band, and the electrical resistance within the cell is minimal. The MPX_3 complexes, however, are non-conducting, and the electron from the lithium has been shown by NMR, Mössbauer, and theoretical calculations to reduce the metal centers to a formal M^0 state [3,4,5]. This lack of conductivity prevents good electron flow through the battery (high internal resistance), and could lower the performance of the cell.

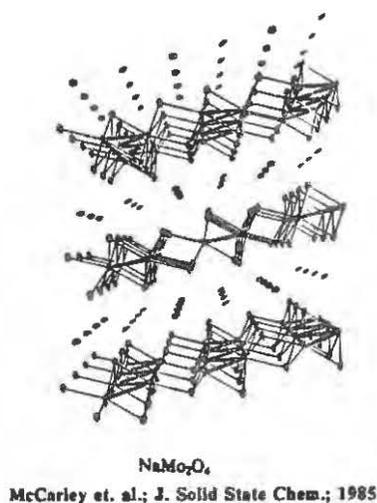


Figure 1

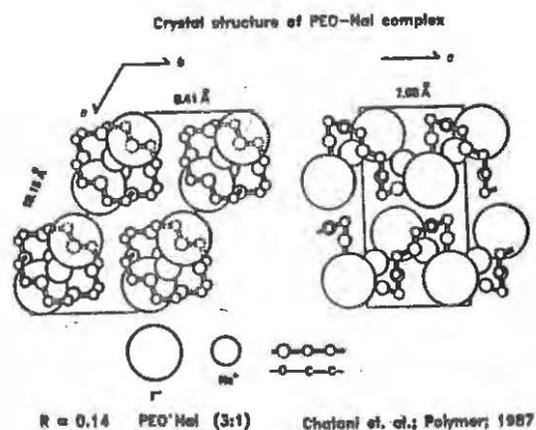


Figure 2

The electrolyte used in MX_2 batteries has traditionally been an alkali metal salt dissolved in an aprotic solvent, such as dioxolane. Recently, this liquid electrolyte has been replaced with a solid polymer electrolyte (SPE). Unlike liquid electrolytes, the SPE needs no containment and is less reactive. There are several polymers which dissolve salts and form conducting complexes [6]. Poly(ethylene oxide) $[(-\text{CH}_2-\text{CH}_2-\text{O}-)_n]$ forms both highly crystalline and amorphous complexes with a wide variety of salts [7]. The crystal structure of a PEO-NaI complex has been determined [8] (Figure 2), and shows the polymer chain coiled around a line of sodium ions, with oxygens coordinated to the sodium. Conduction has been proposed to occur by the motion of the ions through the helical tunnel of the polymer with very little transfer of ions between polymer chains. The conduction in the amorphous SPE is not restrained to one polymer chain and the motion between the chains leads to a higher conductivity. This conductivity has been described by dynamic bond percolation theory [9]. The mobile ions are able to jump between open coordination sites, but the polymer

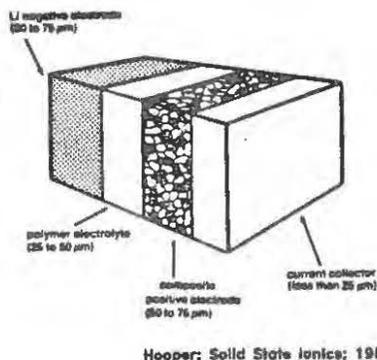


Figure 3

network is also changing with a characteristic regeneration time. If there is little motion in the polymer chain, conduction will be slow, but as polymer motion increases, the conduction also increases. Increased polymer motion can occur by increasing the temperature, or utilizing polymers with lower glass transition temperatures (T_g) [10].

All-solid state batteries have been made using the MS_2 as cathode materials, lithium anodes, and a SPE as electrolyte (Figure 3) [11]. The performance of the cells has been studied, and the cells have been shown to retain their efficiency through many cycles. Although these cells are still at an early stage of development, they appear to be promising candidates for efficient, rechargeable high energy density batteries.

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