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NOVEL HIGH-RATE, ALL SOLID-STATE, SODIUM AND LITHIUM/ORGANOSULFUR BATTERIES

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The pursuit of thin-film solid-state batteries for energy storage applications has greatly accelerated in the past few years. The inherent advantages of all-solid-state cells include negligible self-discharge, long cycle life, high reliability, and virtual absence of container corrosion. Although elegant work on polycrystalline and vitreous electrolytes has led to solid electrolytes with suitable ionic conductivities for battery development, the superior mechanical properties of elastomeric electrolytes combined with the simplicity of fabrication of thin films from these materials, has led to active pursuit of solid-state cells based on solid polymeric electrolytes (SPEs). Although solid polymer electrolytes generally have lower ionic conductivities than their polycrystalline and vitreous counterparts, the ability to cast thin films (10 to 100 μm) from dilute solutions, compensates somewhat for this limitation. The majority of cells based on SPE's have utilized lithium foil negative electrodes and composite positive electrodes containing finely ground intercalation compounds (such as TiS_2) dispersed in the polymeric electrolytes. While many polymeric electrolytes have been described in the literature, the best known SPE is undoubtedly polyethylene oxide (PEO)[1]. The operating temperature of SPE cells generally falls in the range of ambient to 100°C, with the highest levels of performance occurring in the higher temperature regime. Reported results for a number of Li/PEO/X cells have indicated that such solid-state batteries are very close to actual commercialization[2]. The remaining skepticism with regards to SPE-based batteries are the relatively low attainable current densities and associated poor cathode utilization at high drain rates, particularly at low temperatures. This has generally been attributed to the low conductivity of the electrolyte, and consequently a number of groups have been exploring a variety of polymeric materials and/or dopant electrolyte salts in an attempt to increase the conductivity of SPE's. However, recent results in our laboratory have implied that composite cathodes based on intercalation compounds may contribute far more of a limitation to the performance of these cells than has been previously recognized. In fact, by replacing the costly TiS_2 intercalation cathode by an inexpensive polymer/polymer matrix composed of PEO and a solid-redox-polymerization electrode (SRPE), current densities far in excess of those reported for TiS_2 electrodes have been realized. These SRPE's are not "conducting polymers" such as polyacetylene-type materials, but are in fact electronic insulators, necessitating the inclusion of dispersed carbon black in the composite matrix*. Moreover, the gravimetric and volumetric energy and power densities of Li/SRPE

* the exact chemical nature of these materials and their synthesis will be discussed at the presentation.

and Na/SRPE cells are significantly higher than for analogous intercalation compound based cells. Furthermore, the solid-redox-polymerization electrodes (SRPEs) have been shown to have high thermal and chemical stabilities, as well as fast mass transport and electrode kinetics. One battery based on these materials, a Li/PEO/SRPE cell, has achieved over 75 cycles (still cycling), at a sustained power density of 150 W/kg (144 W/l), and a sustained energy density of 260 Wh/kg, with little evidence of deterioration of performance at 77 to 80°C. At 100°C, the Li/PEO/SRPE cell demonstrated a complete discharge cycle (100% of available capacity) at a current density of 10 mA/cm² (12 c rate) and a power density of 2400 W/kg. At ambient temperature, the Li/PEO/SRPE cells could be discharged at current densities of over 250 A/cm². Furthermore, the analogous Na/PEO/SRPE cells have achieved the highest energy and power densities as well as longest cycle lives of any solid state sodium cells to date. The properties of this novel redox system are most clearly illustrated by comparison to the mechanism of protein folding as will be explained in the presentation. The SRPE materials can be generated as 1, 2, or 3-dimensional networks, depending on the mechanical, and electrochemical properties desired. Efforts are currently underway to synthesize a 2-dimensional ladder polymer which will unfold upon discharge of the Li/PEO/SRPE and Na/PEO/SRPE cells.

ACKNOWLEDGEMENT

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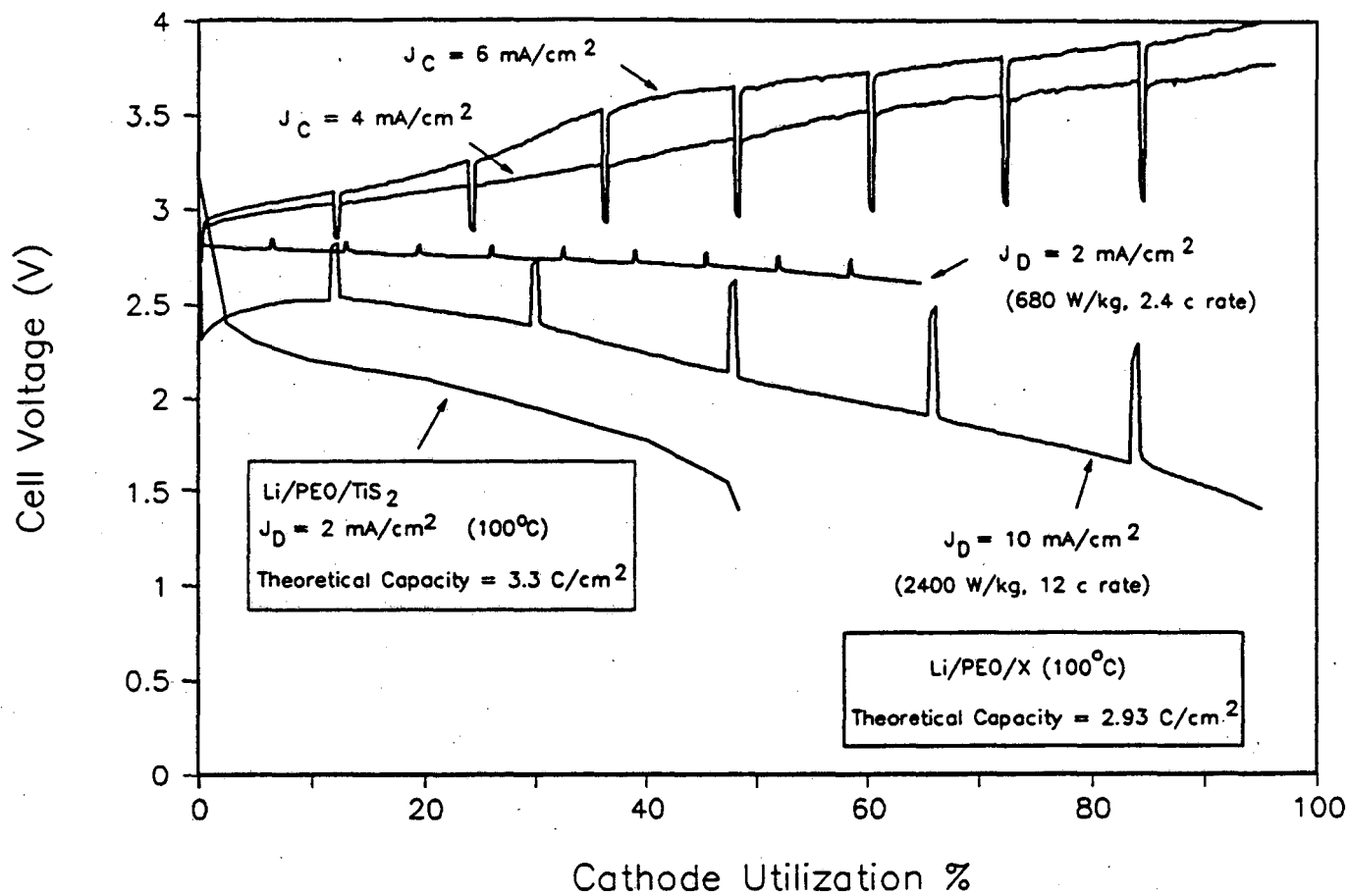


Fig 1. Rate capabilities of all-solid-state Li/PEO/SRPE and Li/PEO/TiS₂ cells.

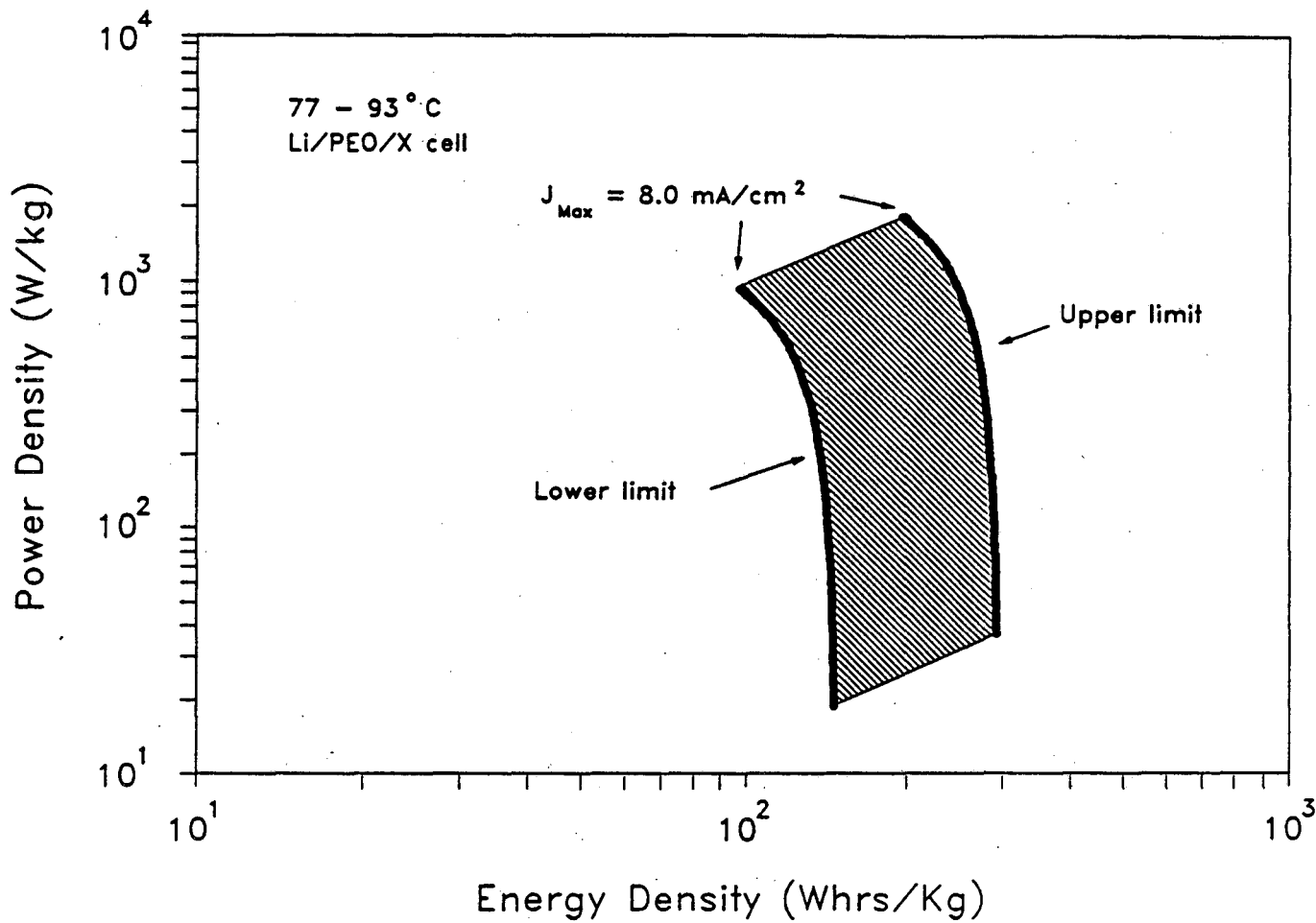


Fig. 2 Gravimetric Ragone plot for Li/PEO/SRPE cells.

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