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Abstract

Research from this laboratory on the sodium/solid polymer electrolyte (SPE) battery is described. Recent results show a performance level that equals or exceeds that of the better-known lithium analogs in terms of rate capability, cycle life and specific power, but at a lower projected cost per kilowatt hour, making sodium/SPE systems attractive for applications such as electric vehicles. Optimization of electrolyte composition and cathodes, using solid redox polymerization electrodes, sodium cobalt oxide or a new manganese oxide, is discussed, and areas for further study are suggested.

Key words: battery, sodium, solid polymer electrolyte, sodium cobalt oxide, manganese oxide.

Introduction

The rapidly growing interest in electric vehicle technologies, and, in particular, advanced batteries, has naturally led to an increased effort in development of the thin film solid polymer electrolyte cell. The advantages of replacing a liquid organic electrolyte with an immobilized polymer are now widely recognized, and include improved safety and interfacial properties as well as ease of battery design and fabrication due to the plasticity of the components [1]. By far the most attention has been directed towards lithium/SPE systems because of their extremely high specific energies. However, the much lower price of sodium ($0.08/equivalent compared to $0.50/equivalent for lithium [2]), provides a compelling rationale for study of the sodium/polymer battery as well. A further cost reduction can be realized by using aluminum current collectors; unlike lithium, sodium does not alloy with aluminum.

The higher equivalent weight and less negative potential vs. S. H. E. of the sodium anode compared to lithium imply a lower specific energy for cells made using the former. However, the use of a thin film electrolyte and the relatively low operating temperature (approximately 85° C) mean that a larger fraction of the theoretical specific energy can be obtained in practical sodium/SPE cells than in the more familiar sodium/sulfur batteries [3], which requires elaborate

engineering. Furthermore, specific energy can be further optimized by judicious choice of cathode material; the options include not only metal sulfide and metal oxide intercalation compounds, but also the newly discovered polyorganodisulfides (solid redox polymerization electrodes or SRPEs [4]).

Performance and safety issues related to Li and Na

The chemistry of sodium is similar to that of lithium. At ambient temperatures, lithium is generally less reactive than sodium, due to the tendency of the former to form compact passivation layers. Because of the greater sensitivity of sodium to oxygen, moisture and impurities, more care must be taken in preparation and handling of electrodes and electrolytes for cells using this metal. This need not be an insurmountable barrier to successful operation, however; recent results in this laboratory have demonstrated cycle lives for sodium-based cells that rival those of the lithium analogs.

At elevated temperatures, the relative reactivities of the two metals are vastly different; molten lithium is far more corrosive than molten sodium, due to the very high free energy of formation of lithium oxide. Above 350° C, sodium oxide is reduced to sodium metal by titanium, whereas titanium oxide is reduced to titanium metal by molten lithium, for example. This suggests that a lithium-based polymer electrolyte cell may be inherently less safe than a sodium-based one in the event of overheating.

The positive electrode

A review by Abraham [5] identified a number of intercalation compounds useful for sodium cells with molten salt, liquid organic or ceramic electrolytes. Several of these are also commonly used in lithium batteries (e.g., TiS_2). However, they tend to intercalate sodium ions over a narrower range of composition than lithium ions, and exhibit decreasing capacity upon cycling. West et al. [6] and Munshi et al. [7] pioneered the concept of the sodium/SPE battery using amorphous MoS_3, $Na_xCr_3O_8$, and vanadium oxide cathodes. While these systems did work, they fell far short of EV performance objectives in terms of specific energies, cycle life and specific power. Identification of new cathode materials with higher capacities, better inherent reversibility and high rate capability for sodium/SPE cells was an early goal of this laboratory. Table I summarizes the characteristics of a sodium cobalt oxide, a sodium manganese oxide and the polyorganodisulfide of dimercaptothiadiazole studied at Lawrence Berkeley Laboratory.

The P2 sodium cobalt bronze (Na_xCoO_2) has a layered structure, with trigonal prismatic sites for sodium ions between the layers (Figure 1a) [8]. It is prepared in the partially discharged state as $Na_{0.7}CoO_2$ via a high temperature synthesis. After the cell is initially charged to a nominal composition of $Na_{0.3}CoO_2$, up to 0.6 Na/Co can be inserted from 4.0-1.5 V vs. Na. The sloping voltage profile is

characteristic of a single phase system. Cells with sodium anodes, poly(ethylene oxide) separators and P2 Na_xCoO_2 composite cathodes typically achieve 100% D. O. D. at 0.5-1 mA/cm^2 and can be charged at the same rate [9]. Very high practical power densities of 335 W/L for continuous operation, and up to 2.7 kW/L for pulses of several minutes, have been calculated based upon the high rate capability of this system. Na/PEO/Na_xCoO_2 cells have also been cycled 200 times at 0.5 mA/cm^2. The remarkable reversibility of the P2 sodium cobalt bronze has been attributed to the absence of structural changes during intercalation/de-intercalation processes [10]. These results clearly show that performance need not be compromised by substituting sodium for lithium in polymer cells.

The high cost and relative scarcity of cobalt oxide starting materials may mean that the P2 sodium cobalt bronze is not practical for use in EV applications. Manganese oxides, however, are very inexpensive and widely available, and therefore are attractive for large-scale battery use. Lithium manganese oxide spinels are now being developed for lithium and lithium-ion cells [11], but do not insert sodium to any appreciable extent unless the lithium is removed, allowing a phase transition to a layered structure[12]. No sodium manganese oxide spinel analogs exist; the large sodium ion is not readily accommodated into this rather crowded structure. Furthermore, selection of a manganese oxide suitable for polymer cells is complicated by the large number of structures available and the

phase instability of this system. A stable sodium manganese oxide cathode with high capacity and voltage vs. Na has recently been discovered in this laboratory [13]. Orthorhombic Na_xMnO_2, prepared at high temperatures with a nominal composition of $Na_{0.44}MnO_2$, has an unusual three-dimensional structure with two types of large tunnels (Figure 1b) [14]. The range of intercalation is from x=0.2 to x=0.75 or approximately 0.55 Na/Mn over a range of 3.45-2.2 V vs. Na (open circuit). Again, the sloping voltage profile is characteristic of a single phase system; a result confirmed with x-ray diffraction studies. 100% utilization can be obtained at discharge rates of 0.1 mA/cm^2 and Na/PEO/Na_xMnO_2 cells have been cycled 60 times at this rate. While the performance is not as impressive as the sodium cobalt bronze, it represents a significant improvement over other manganese oxides in either lithium or sodium polymer cells. Futher improvement can be realized by doping the orthorhombic structure with other metals such as iron. One such material shows an improved rate capability (100% D. O. D. at 0.2 mA/cm^2) and has been cycled 170 times at 0.1-0.5 mA/cm^2 [15].

The orthorhombic sodium manganese oxide may also be used in lithium polymer cells after chemical treatment to remove mobile sodium ions or to exchange sodium ions with lithium. Slightly more lithium than sodium is inserted, resulting in a capacity of 180 mAh/g over a range of 3.7-2.5 V vs. Li (open circuit). Cells with lithium anodes, polymer electrolytes and Na_xMnO_2

cathodes have been discharged 90 times at 0.1-0.2 mA/cm^2, with improved capacity retention over lithium/polymer cells with lithium manganese oxide spinel cathodes [15]. The excellent reversibility, relatively good rate capability and remarkable stability of orthorhombic Na_xMnO_2 set it apart from other manganese oxides, which are notoriously difficult to use in secondary battery systems.

Other cathode systems which have shown promise in sodium polymer cells are the SRPEs, polyorganodisulfides with formula $-(SRSSRS)_n$. These disulfide-linked polymers undergo a reversible reduction to thiolate anions at moderately high voltages versus sodium or lithium. Discharge profiles are typically flat, and the electrochemical properties are dependent upon the R group in the polymer [4]. Sodium/SPE cells with the polymer of dimercaptothiadiazole (Figure 1c) have been cycled up to ninety times at 0.25 mA/cm^2 [16]. Especially noteworthy features of the SRPEs are their low cost, low toxicity and their exceptionally high capacities, leading to very high specific energies in sodium cells,.

The polymer electrolyte

The criteria for the electrolyte in sodium cells are the same as for lithium; a wide voltage window, stability towards the alkali metal, high conductivity, good mechanical properties and ease of fabrication. The greater reactivity of sodium restricts the selection of electrolyte even further. The addition of plasticizers to polymer electrolytes to improve conductivity is likely to result in greatly reduced

cycle life due to corrosion at the sodium electrode. In contrast, completely dry and plasticizer-free electrolytes consisting of poly(ethylene oxide) and sodium perchlorate [17] have been found to have reasonably good stability towards sodium, allowing a hundred or more deep discharge cycles to be obtained readily.

Lithium-containingPEO electrolytes have been extensively studied [18-21] but much less is known about the corresponding sodium-PEO complexes. A rigorous study of the conductivities and transport properties of $P(EO)_xNaCF_3SO_3$ and $P(EO)_xNaClO_4$ electrolytes is now underway in this laboratory. Careful measurement of sodium diffusion coefficients, using a restricted diffusion method, and AC impedance measurements show that a composition of $P(EO)_{20}NaCF_3SO_3$ should give optimum results. Furthermore, sodium ion transference numbers measured for $P(EO)_xNaCF_3SO_3$ are much less than 1, and decrease considerably as x decreases; e.g., ion aggregation increases as the sodium trifluoromethanesulfonate concentration increases. (This effect is weaker in sodium perchlorate- poly(ethylene oxide) complexes).

This suggests that better results should be obtained with more dilute concentrations of sodium salt in PEO. Figure 2 shows that, indeed, the rate capability of $Na/PEO/Na_xCoO_2$ cells is markedly improved when $P(EO)_{20}NaCF_3SO_3$ is used instead of $P(EO)_8NaCF_3SO_3$.

For reasons of thermal management, it is desirable to lower the operating temperature of sodium/polymer cells below the 80-90° C used now. The conductivities and diffusion coefficients of sodium polymer electrolytes are generally higher than those of lithium polymer electrolytes. It might therefore be possible to lower the operating temperature as much as 10-20° C without using plasticizers or compromising power densities unduly, particularly if electrolyte compositions and salts are optimized. Lithium bis(trifluoromethanesulfonate) imide (LiTFSI) has been used for this purpose in lithium cells successfully; NaTFSI may have a similar effect in sodium cells, but has not yet been thoroughly investigated.

The negative electrode

Table 2 summarizes characteristics of anode materials used in polymer batteries. While it is evident that the gravimetric capacity of sodium, although quite high, is substantially less than that of lithium, the volumetric capacity is less severely penalized. The rather low melting point of sodium poses a more difficult problem in terms of thermal management of batteries for electric vehicles, however. A sodium-lead alloy with a very high melting point, $Na_{15}Pb_4$, has been used successfully in both liquid electrolyte [22] and polymer electrolyte [9] cells. Reversible sodium insertion into disordered carbons [23] using polymer electrolytes provides another attractive alternative, that of the solid state sodium

ion rocking chair battery. For both the carbon and sodium-lead alloy, gravimetric capacities are severely compromised, however. A recent report of new disordered carbons with high lithium ion storage capability [24] suggests that substantial improvements may be made in the carbon electrode. If the specific energy problem can be successfully addressed, a sodium ion rocking chair battery may solve the problem of thermal management. Because sodium ions are generally more conductive than lithium ions, a sodium ion cell is expected to have higher power densities than the lithium ion analog as well.

Cell cycling

Deep discharge cycling has been obtained on sodium/polymer batteries with Na_xCoO_2, Na_xMnO_2, doped Na_xMnO_2 and poly(dimercaptothiadiazole) electrodes. The number of cycles obtained range from 60-200 depending upon the cathode used and the discharge rate. Capacity fading is evident in all of the cells cycled so far. Although this suggests that the Na/PEO interface is responsible, cells with a positive/positive configuration (e.g., Na_xCoO_2/PEO/Na_xCoO_2, Na_xMnO_2/PEO/Na_xMnO_2) show similar losses upon cycling. Four probe dc experiments on Na/PEO/Na_xCoO_2 cells show no increase in resistance at the Na/PEO interface with time or with cycling [9]. While it is certainly true that sodium reacts with the polymer electrolyte, as does lithium, the interfacial layer appears to be reasonably conductive and stable with time and passage of current.

A possible explanation for loss of capacity in intercalation electrodes is an irreversible phase transition upon cycling. X-ray diffraction experiments reveal no such structural changes for cycled sodium cobalt bronze or sodium manganese oxide electrodes, however. Both of these materials are very oxidizing in the charged state, and may react slowly with the electrolyte or other components in the cell. (Cyclic voltammetry indicates that PEO-$NaCF_3SO_3$ is stable to 4 V, but will not detect slow reactions). Better capacity retention is obtained for Na_xCoO_2 cells when the voltage is restricted below 3.7 V upon charge [15].

Disconnection of the particles in the positive electrode due to volume changes upon intercalation or de-intercalation [25] can contribute to loss of capacity upon cycling in some instances. This effect will be highly system specific; volume changes may be more severe in layered compounds such as the cobalt oxide than in tunnel structures like the orthorhombic manganese oxide.

Mass transfer effects and salt precipitation due to polarization may have a temporarily deleterious effect upon performance as well. Use of $P(EO)_{20}NaX$ rather than the more concentrated electrolytes, judicious use of rest periods [26] between half-cycles and improved fabrication of cathodes should therefore lead to better capacity retention and longer cycle life.

Conclusions

It has now been shown that the performance of sodium/SPE system can equal, or in some cases, even exceed the performance of the lithium analog. While specific energies are not as large as in the lithium case, they are high enough for EV applications, particularly when the P2 sodium cobalt bronze, orthorhombic sodium manganese oxide or SRPEs are used as cathodes. Power densities are expected to be greater for sodium systems due to the enhanced conductivity of this ion in polymer electrolytes; this feature is readily demonstrated in $Na/PEO/Na_xCoO_2$ cells. The study of sodium/SPE batteries can lead to improvements in the lithium cells and vice versa. The orthorhombic sodium manganese oxide discovered in the course of this study has proven to be useful in lithium cells, for example. Advances in the field of lithium and lithium ion batteries may be "borrowed" for use in sodium/SPE cells, leading to rapid progress. Examples of this are the development of new, highly conductive salts for polymer electrolytes and new carbons for use as anodes. Better understanding of cathode, electrolyte and interfacial characteristics should further aid advancement. The recently demonstrated high level of performance and projected low cost of sodium/polymer cells makes them attractive alternatives to lithium systems for electric vehicle applications.

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Table 1. Characteristics of Positive Electrode Materials in Sodium/Polymer Batteries.

Cathode material	Type and Structure	Capacity mAh/g[a]	Average V vs. Na	Theoretical Specific Energy, Wh/kg	Theoretical Energy Density, Wh/L
P2 Na_xCoO_2	intercalation, layered structure	165	2.8	440	1600
Na_xMnO_2	intercalation, tunnel structure	163	2.9	420	1410
Dimercapto-thiadiazole polymer	polyorgano-disulfide (SRPE)	362	2.7	746	1121

a) Capacity calculated based on the fully charged state.

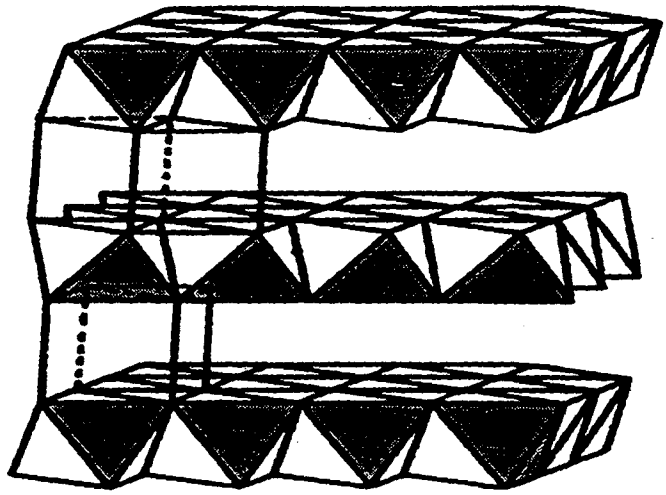
Table 2. Characteristics of some Anode Materials

Anode	Capacity, Ah/g	Capacity, Ah/cc	Melting Point, ° C
Na	1.19	1.13	97
$Na_{15}Pb_4$	.325	0.89	386
NaC_{24}	.086		
Li	3.86	2.05	180

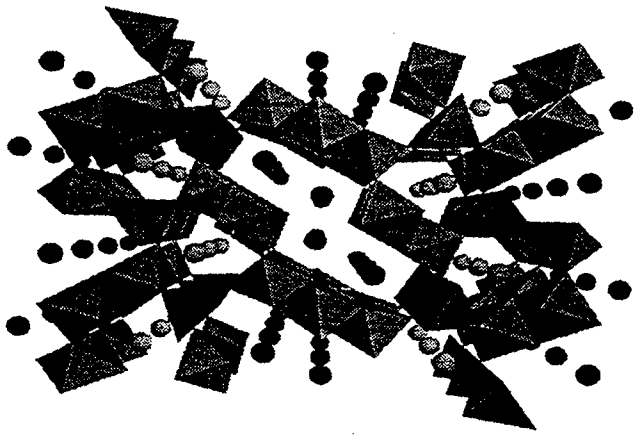
Figure Captions

1) The structure of: a) P2 Na_xCoO_2, taken from reference 8: b) orthorhombic Na_xMnO_2 and c) dimercaptothiadiazole.

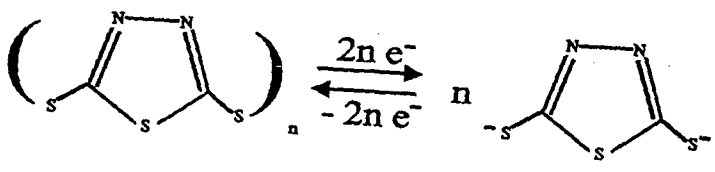
2) Discharges at different rates for a) $Na/P(EO)_8NaCF_3SO_3/Na_xCoO_2$ cells and b) $Na/P(EO)_{20}NaCF_3SO_3/Na_xCoO_2$ cells. Better utilization is obtained at higher rates for the cells with $P(EO)_{20}NaCF_3SO_3$ electrolyte.



(a)

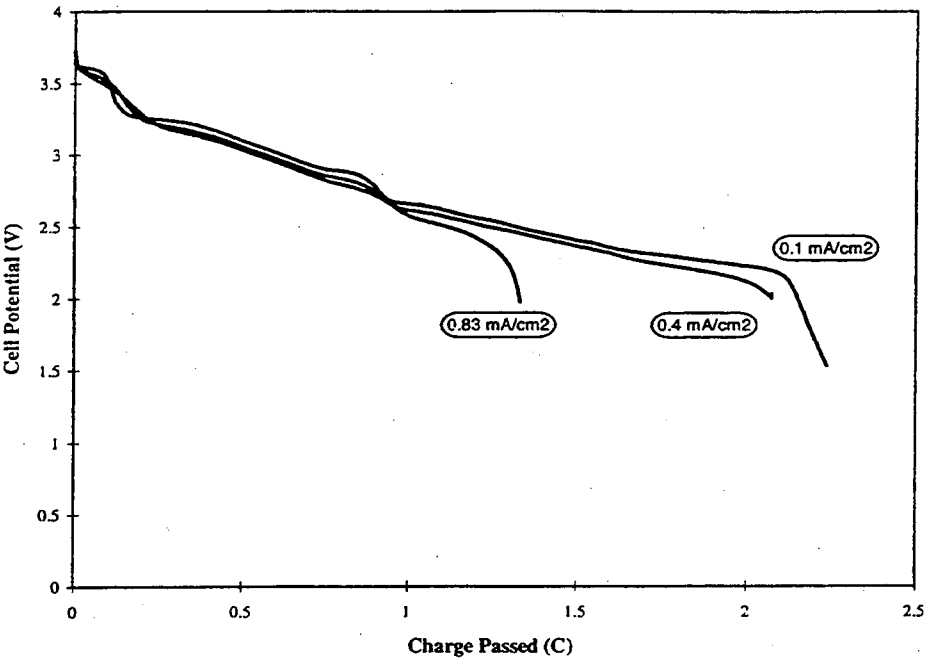


(b)

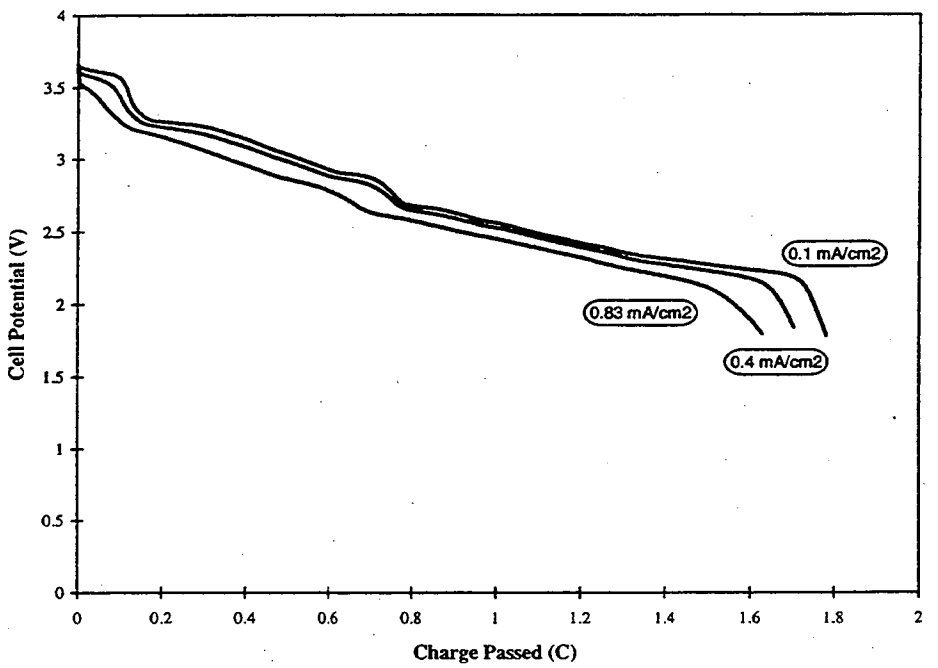


(c)

Figure 1


Cell Potential (V)
Charge Passed (C)
0.1 mA/cm2
0.83 mA/cm2
0.4 mA/cm2
0
0.5
1
1.5
2
2.5
3
3.5
4

(a)


Cell Potential (V)
Charge Passed (C)
0.1 mA/cm2
0.83 mA/cm2
0.4 mA/cm2
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
0.5
1.5
2.5
3
3.5
4

(b)

Figure 2

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