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Journal

Journal of the Electrochemical Society, 140(12)

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Publication Date

1993-08-19



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials Sciences Division

Submitted to Journal of the Electrochemical Society

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August 1993



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Electrochemical Insertion of Sodium into Carbon

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This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Transportation Technologies, Electric & Hybrid Propulsion Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

potentials dropped rapidly upon passage of current, and a cutoff of 0.03 V was used to prevent interference from sodium plating (expected to occur at slightly below 0 V in operating sodium cells). The extent of sodium insertion was calculated from the time and amount of current passed. Complexes of approximate compositions NaC_{30} and NaC_{15} were formed for petroleum coke and Shawinigan black, respectively, but the maximum for graphite was only about NaC_{70} , in contrast to lithium into graphite (LiC_6) and petroleum coke (LiC_{12}). True reductive intercalation in Li/graphite cells occurs only below about 0.4 V⁶; thus the corresponding process in sodium cells is expected to occur only below 0.1 V. (The standard reduction potentials for Li^+/Li and Na^+/Na are -3.0 and -2.7 V, respectively). In other words, most of the reductive insertion process is expected to occur *below the sodium plating potential in Na/graphite cells, and thus cannot be observed*. For disordered carbons, insertion of sodium occurs at a higher voltage than graphite, and can proceed farther.

Figure 1 also shows that the extent of reaction depends very strongly upon the particle size in disordered carbons. Petroleum coke used as received (average particle size, 70 μm) does not insert sodium ions appreciably, but forms compounds of approximate stoichiometry NaC_{30} after it has been ground to 1 μm . Insertion into Shawinigan black, a very fine (sub-micron particle size) carbon powder proceeded the furthest, to NaC_{15} . This suggests that the inserted sodium may, at least in part, be associated with sites on the surfaces of the particles rather than being truly intercalated between layers in the disordered carbons; i.e., supercapacitor behavior is exhibited⁷.

Figure 2a shows several cycles of a Na/P(EO)₈NaTf/petroleum coke cell, discharged at various rates. Approximately 20% of the sodium ions originally inserted into petroleum coke cannot be removed upon the first charge; however, no further losses are seen on subsequent cycles. This is similar to the situation with lithium and petroleum coke, and has been attributed to an irreversible reaction of alkali metal ions and formation of a protective layer on the carbon electrode⁶. In Na/petroleum coke cells, insertion was reversible (except for the loss noted above) when either PEO or dimethoxyethane based electrolytes (Figure 2b) were used. When propylene carbonate, ethylene carbonate, γ -butyrolactone or mixtures of these solvents were used instead, the cells could not be recharged. Apparently, passivation occurs only in the presence of ether-containing electrolytes. Interestingly, Li/PEO/graphite and Li/PEO/petroleum coke cells also show evidence of continuous decomposition (irreversibility) upon intercalation, rather than passivation. This may reflect the greater extent of insertion of lithium ions into carbon and the fact that more strongly reducing compounds are formed. Irreversibility was also seen in the Na/PEO/Shawinigan black cells and may be occurring for the same reasons.

An unoptimized rocking chair cell consisting of a petroleum coke anode, P(EO)₈NaCF₃SO₃ separator and Na_{0.6}CoO₂ cathode was assembled and cycled (Figure 3) at moderate rates. Only half the theoretical capacity of the cathode can be utilized in this configuration (Na_{0.6}CoO₂ is in the halfway discharged state and exhibits a sloping discharge profile vs. Na), but the results clearly illustrate the viability of such a system. Polyorganodisulfides⁸ may be a better choice for cathodes, because they exhibit flat discharge profiles vs. Na and have extremely

high capacities. Optimization of a sodium ion rocking chair cell will require not only proper choice of cathode, anode and electrolyte but also careful balancing of the electrode capacities to compensate for the initial loss of ions upon charge. It is now apparent, however, that the concept of the rocking chair battery need not be limited to lithium ion systems alone.

Conclusions

Carbon undergoes reversible electrochemical insertion of sodium ions, a process that may be exploited in sodium ion rocking chair batteries. A maximum composition of NaC_{15} has been achieved, and reversible insertion to NaC_{24} for petroleum coke in cells with ether-based electrolytes has already been demonstrated. An unoptimized system with a petroleum coke anode, polyethylene oxide separator and sodium cobalt bronze cathode could be charged and discharged successfully, and suggestions for improved performance have been given.

Acknowledgment

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Transportation Technologies, Electric & Hybrid Propulsion Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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Figure Captions

1. Discharges ($50 \mu\text{A}/\text{cm}^2$) of $\text{Na}/\text{P}(\text{EO})_8\text{NaCF}_3\text{SO}_3/\text{C}$ cells heated to 86°C . The spikes in the profiles are due to periodic current interrupts to assess the cell polarization.
2. a) Cycling of a $\text{Na}/\text{P}(\text{EO})_8\text{NaCF}_3\text{SO}_3/(\text{ground})$ petroleum coke cell at $0.05\text{-}0.2 \text{ mA}/\text{cm}^2$ (discharge) and $0.025 \text{ mA}/\text{cm}^2$ (charge). Temperature = 86°C . The gray line indicates the first cycle, and the dashed line, the third discharge. The voltage instabilities evident in cycles 6 and 7 are probably due to dendrite formation. b) first cycle of a $\text{Na}/\text{DME}, \text{NaClO}_4/(\text{ground})$ petroleum coke cell at $50 \mu\text{A}/\text{cm}^2$. Temperature = 21°C . The spikes in the profiles are due to current interrupts to estimate the cell polarization.
- 3) First cycle of a $\text{Na}_{0.6}\text{CoO}_2/\text{P}(\text{EO})_8\text{NaCF}_3\text{SO}_3/(\text{ground})$ petroleum coke cell, $0.1 \text{ mA}/\text{cm}^2$ discharge, $0.25 \text{ mA}/\text{cm}^2$ charge. Temperature = 100°C . The spikes in the profiles are due to current interrupts to estimate cell polarization.

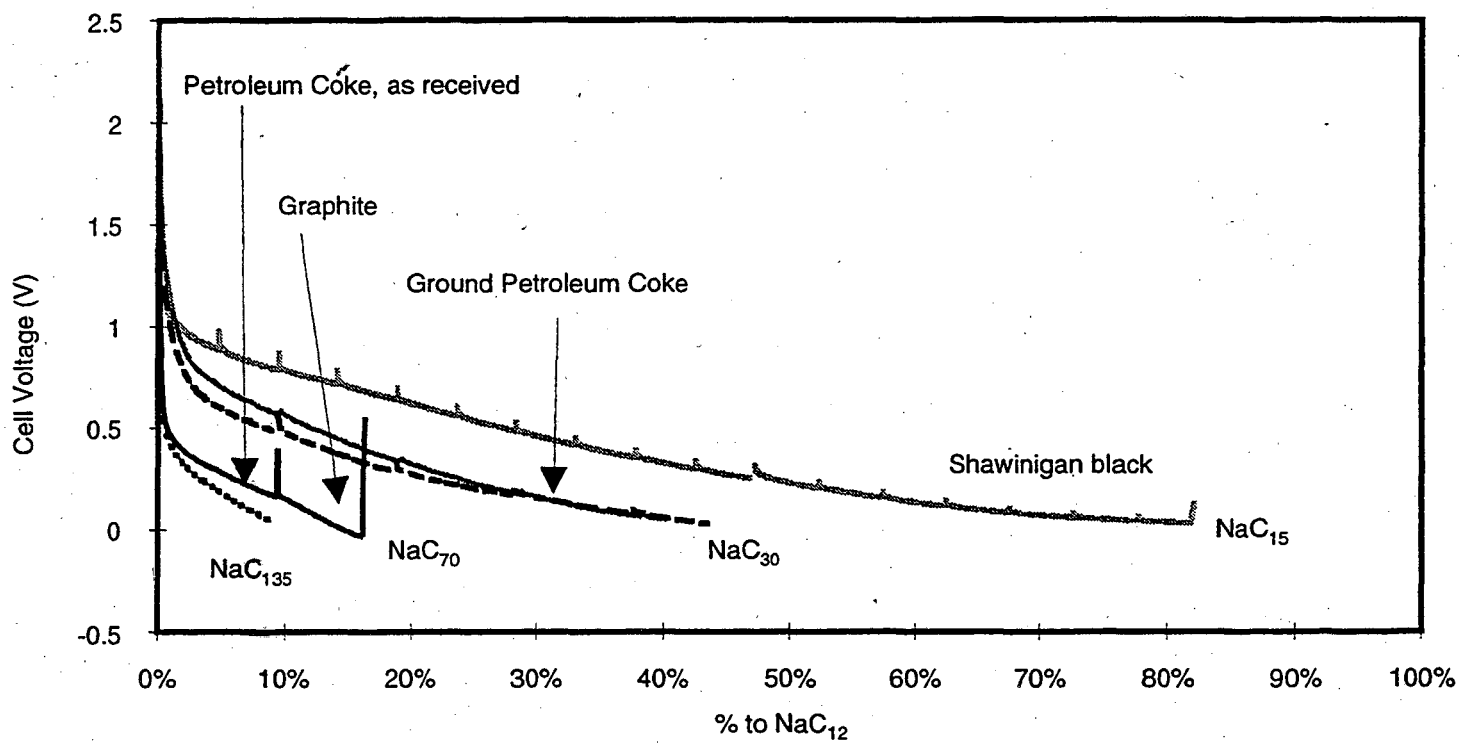
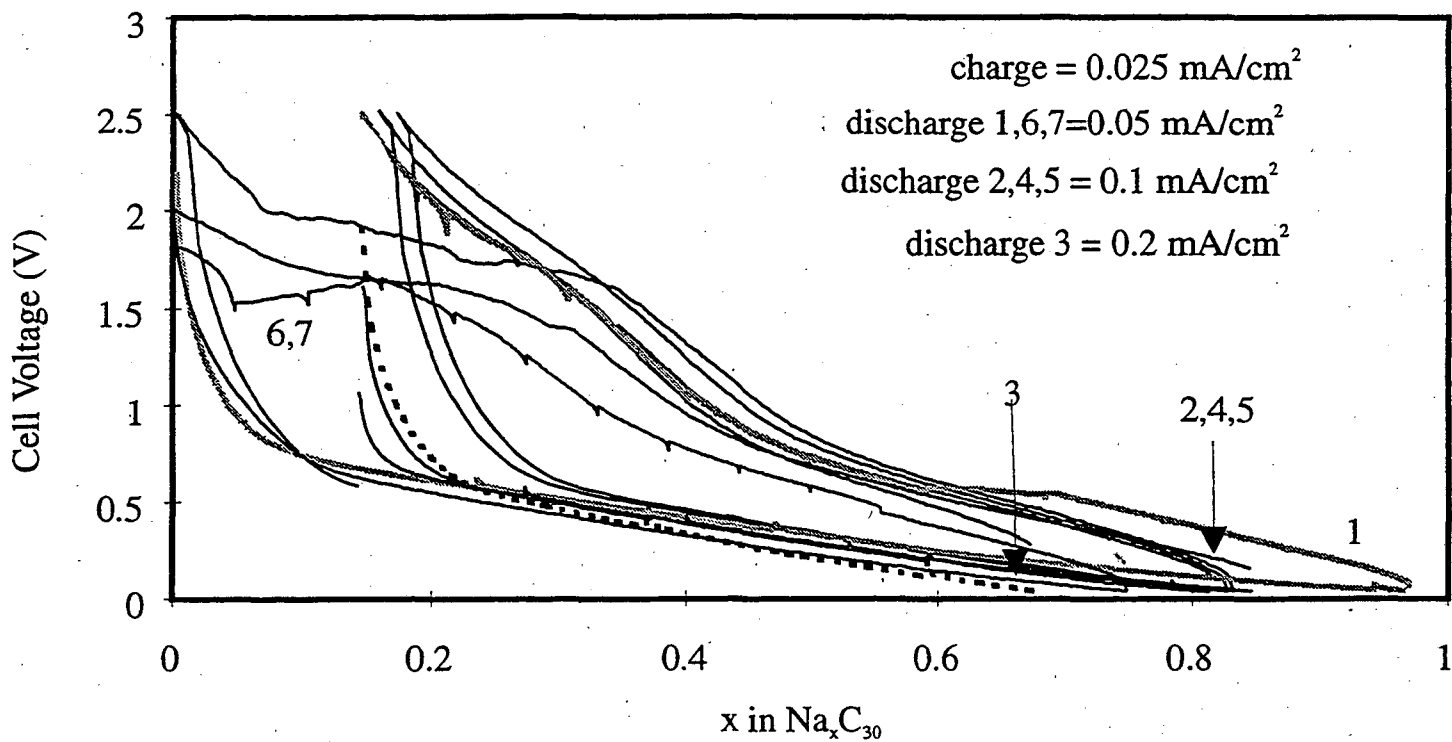
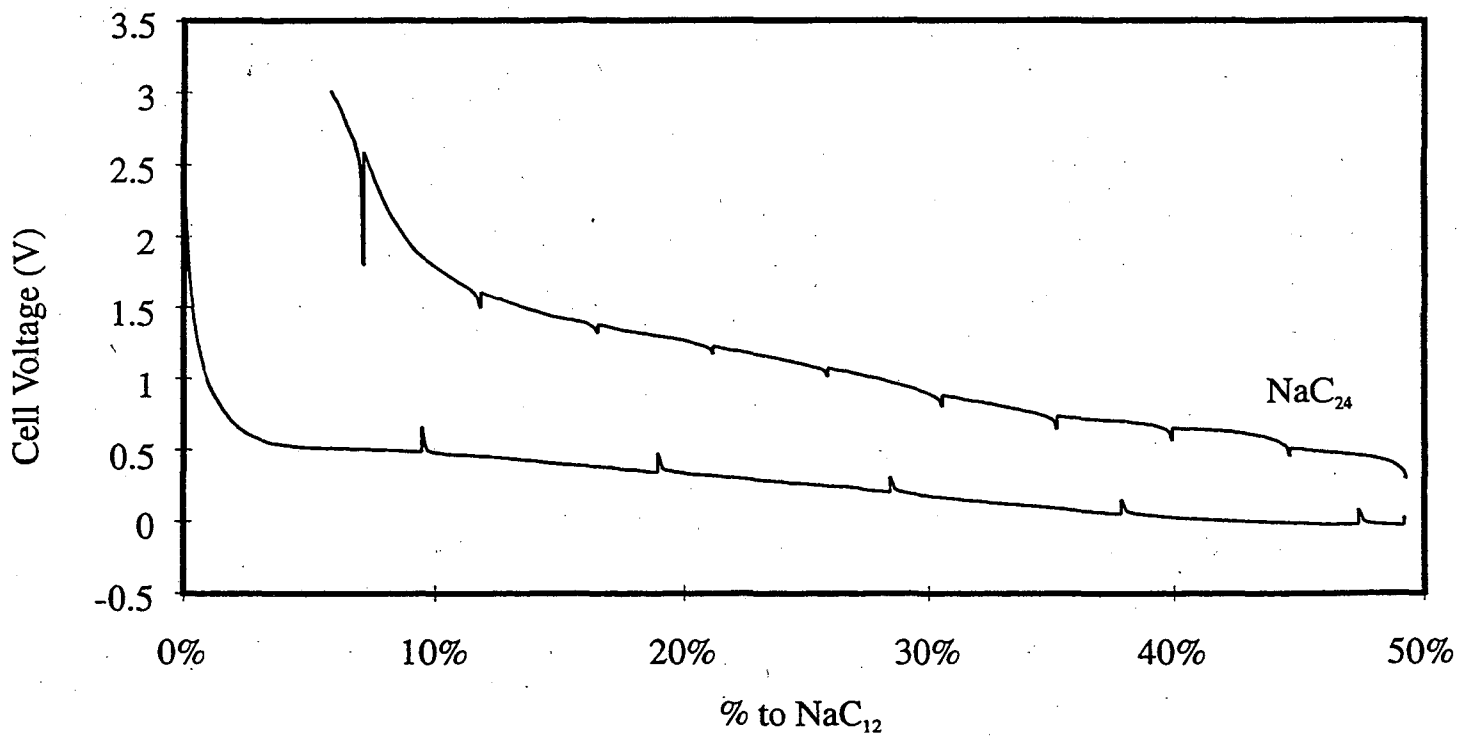


Figure 1



a.



b.

Figure 2a and b

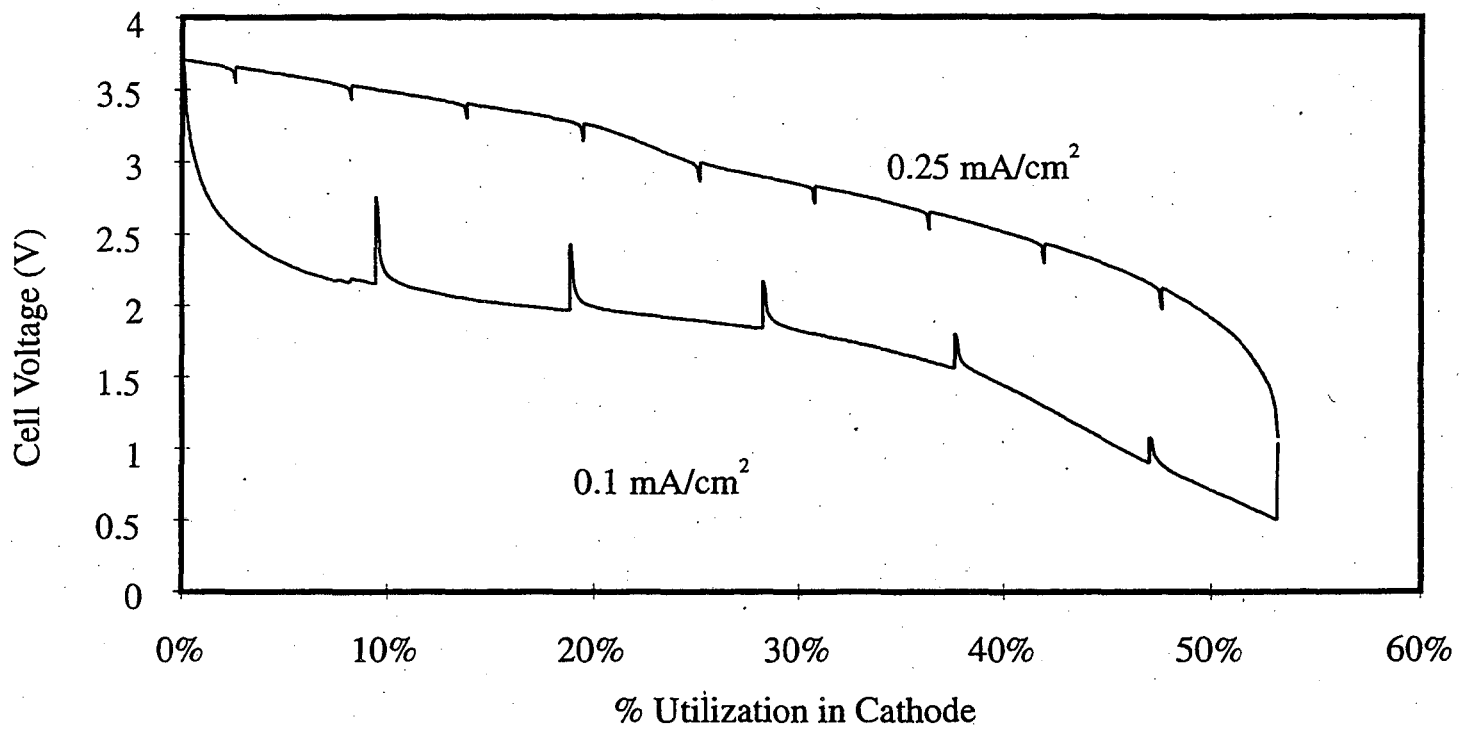


Figure 3

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