REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

AD-A219 428

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	31 Dec 81	Final

4. TITLE AND SUBTITLE

NEW MATERIALS FOR ELECTROCHEMICAL CELLS

5. FUNDING NUMBERS

61102F
2303/A1

6. AUTHOR(S)

Prof. John B. Goodenough
Dr. Peter G. Dickens

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of Oxford
Inorganic Chemistry Laboratory,
South Parks Road,
Oxford, OX1 3QR, England

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR
BLDG 410
BAFB DC 20332-6448

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

AFOSR-77-3402

DTIC ELECTE MAR 1 6 1990 S D

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

[illegible] release: distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Determination of the thermochemical, structural and basic electrochemical properties of mixed electronic/ionic conductors was successfully carried out on the following systems: H_xMoO_3, $Li_xV_2O_5$, H_xWO_3, and Li_xMoO_3. Attempts to design new protonic and Li^+ ion conductors have opened up two fields: One is the recognition of particle hydrates as protonic electrolytes capable of fabrication into dense ceramics by cold pressing; we have obtained room-temperature H^+ ion conductivity approaching 10^{-2}/ohm/cm^{-1} in cold-pressed $Sb_2O_5 \cdot 5.4H_2O$. The other is the use of low-temperature chemical and electrochemical techniques to prepare new materials not attainable with high-temperature techniques. With this method we have prepared $Li/Li_{1-x}CoO_2$ cells having open-circuit voltages in excess of 4 V. We have also initiated studies into composite electrolyte/electrode materials using room-temperature molten salts immobilized by insertion-compound electrode materials.

14. SUBJECT TERMS	15. NUMBER OF PAGES
	184
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
unclassified	unclassified		

NSN 7540-01-280-5500

Standard Form 298 (890104 Draft)
Prescribed by ANSI Std. 239-18
298-01

90 01 04 073

FINAL REPORT

NEW MATERIALS FOR ELECTROCHEMICAL CELLS

JOHN B. GOODENOUGH

PETER G. DICKENS

AFOSR-77-3402

UNIVERSITY OF OXFORD
INORGANIC CHEMISTRY LABORATORY
SOUTH PARK ROAD
OXFORD, OX1 3QR, ENGLAND

1 JANUARY 1978 - 31 DECEMBER 1981

COMPLETED PROJECT SUMMARY

1. TITLE: New Materials for Electrochemical cells

2. PRINCIPAL INVESTIGATORS: Prof. John B. Goodenough
Dr. Peter G. Dickens
Inorganic Chemistry Laboratory,
University of Oxford,
Oxford. OX1 3QR
England.

3. INCLUSIVE DATES: 1 January 1978 - 31 December 1981

4. GRANT NUMBER: AFOSR - 77-3402, 2303/A1

5. COSTS AND FY SOURCE: $23,640, FY78; $32,128, FY79; $30,000, FY80; $32,580 FY81

6. SENIOR RESEARCH PERSONNEL: K. Mizushima
O. Nakamura
Dr. R. C. T. Slade
T. Takeda
Dr. P. J. Wiseman

7. JUNIOR RESEARCH PERSONNEL: D. P. Birkett
J. J. Birtill
M. F. Cross
W. H. England
S. J. French
S. J. Hibble
A. T. Hight
R. H. Jarman
M. F. Pye
F. J. Reynolds

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3 "Thermochemistry of Hydrogen Molybdenum Bronze Phases H_xMoO_3, J. J. Birtill and P. G. Dickens, J. Solid State Chemistry 29, 367 (1979)

4 "NMR Study of Hydrogen Molybdenum Bronzes: $H_{1.7}MoO_3$ and $H_{0.36}MoO_3$", R. C. T. Slade, T. K. Halstead and P. G. Dickens, J. Solid State Chem 34, 183 (1980)

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Not attached

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"New Solid Proton Conductors", M. G. Cross, D.J. Dzimitrowicz, W. A. England and P. J. Wiseman, N.R.D.C. Provisional patent (1980)

"Synthetic Procedure for High Area Oxide Cathodes", K. Mizushima and P. J. Wiseman, A.E.R.E. Harwell Provisional Patent (1980)

10. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The research had two main aims (i) Determination of the thermochemical, structural, and basic electrochemical properties of mixed electronic/ionic conductors and (ii) design, preparation and characterization of new ionic conductors, both electronic insulators for electrolytes and electronic conductors for battery cathodes and display.

The first objective was succesfully carried out on the hydrogen molybdenum bronzes H_xMoO_3, the system $Li_xV_2O_5$, the hydrogen tungsten bronzes H_xWO_3, and the system Li_xMoO_3. This work was supplemented by NMR studies on hydrates.

Work toward the second objective also concentrated on H^+-ion and Li^+-ion conductors. We were able to demonstrate that classical ion-exchange materials form a broad class of H^+-ion conductors that can be separated into two groups; framework hydrates and particle hydrates. Moreover we showed that the best protonic conduction would be found in hydrates of highly acidic or highly basic oxides, the highest water content compatible with retaining a solid representing the optimum condition. We also showed that particle hydrates can be formed into dense ceramics of large surface area by cold pressing, and that under a controlled H_2O atmosphere the ceramic remains solid and retains it's water to nearly 100^oC. Our best H^+-ion conductor was antimonic acid, a framework hydrate, that was fabricated as a particle hydrate and cold pressed to $Sb_2O_5 \cdot 5.4H_2O$. At room temperature, the H^+-ion conductivity approached 10^{-2} $ohm^{-1} cm^{-1}$.

We also demonstrated that important new materials can be fabricated by low-temperature techniques, including room-temperature electrochemistry. Our first exploitation was the preparation of the systems $Li_{1-x}CrO_2$, $Li_{1-x}CoO_2$ and $Li_{1-x}NiO_2$. Most work has been done on the latter two systems, which give over 4V when used as a cathode against elemental lithium as the anodes. Work on the system $Na_{1-x}CoO_2$ proved that Na^+ ions have a preference for trigonal prismatic sites that reduces the solid-solution range. For the Lithium systems the range is $0 \leq x < 1$.

We also concluded that the best composite electrodes will consist of a molten salt that is immobilized by a porous (pressed-particles) insertion-compound electrode; these composites may need to be separated by a solid electrolyte.

An investigation of $LiBr.nH_2O$, $1<n<2$, with and without Al_2O_3 particles demonstrated that molten salts can be immobilized if hydrogen-bond bridges between particles can be formed. However, we need to eliminate the water, and we have begun to investigate anhydrous salts molten at room temperature.