Lawrence Berkeley National Laboratory

Recent Work

Title

DEVELOPMENT OF A HIGH RATE INSOLUBLE ZINC ELECTRODE FOR ALKALINE BATTERIES

Permalink

<https://escholarship.org/uc/item/6x1626h2>

Author

Charkey, A.

Publication Date

1982-04-01

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT DIVISION

RECEIVED
LAWRENCE
BERKELEY LABORATORY

AUG 17 1982

LIBRARY AND
DOCUMENTS SECTION

DEVELOPMENT OF A HIGH RATE INSOLUBLE ZINC
ELECTRODE FOR ALKALINE BATTERIES

Alan Charkey

April 1982

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782.*

LBL-14674
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

DEVELOPMENT OF A HIGH RATE INSOLUBLE
ZINC ELECTRODE FOR ALKALINE BATTERIES

Alan Charkey
Energy Research Corporation
3 Great Pasture Road
Danbury, CT 06810
Purchase Order: 4506710

April 1982

Sponsor: Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Systems Research, Energy Storage Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

TABLE OF CONTENTS

	<u>Page No.</u>
<u>SUMMARY</u> -----	1
1.0 <u>INTRODUCTION</u> -----	3
2.0 <u>TECHNICAL DISCUSSION</u> -----	4
2.1 PREPARATION OF EXPERIMENTAL MATERIALS -----	4
2.2 SOLUBILITY DETERMINATIONS -----	5
2.3 EXPERIMENTAL EQUIPMENT -----	6
2.4 ELECTROCHEMICAL EVALUATIONS -----	7
2.4.1 <u>Efficiency Tests</u> -----	7
2.4.2 <u>Cyclic Voltammetry</u> -----	10
2.4.3 <u>Cathodic Polarization Studies</u> -----	13
2.5 CELL TESTS -----	15
3.0 <u>CONCLUSIONS</u> -----	18

LIST OF TABLES

<u>Table No.</u>		<u>Page No.</u>
1	SOLUBILITY DATA -----	19
2	EFFECT OF KOH CONCENTRATION ON THE SOLUBILITY OF DOPED ZnO -----	20
3	EFFICIENCY AND ELECTROCHEMICAL SOLUBILITY DATA -	21
4	NEW ZnO COMPOUNDS UNDER STUDY -----	22
5	ADDITIONAL ZnO COMPOUNDS UNDER STUDY -----	23

TABLE OF FIGURES

<u>Figure No.</u>		<u>Page No.</u>
1	POLARIZATION CELL -----	24
2	CYCLIC VOLTAMMOGRAM IN 1.95m KOH + Zn^{2+} CYCLE #25 -----	25
3	CYCLIC VOLTAMMOGRAM IN 8.8m KOH CYCLE #25 -----	26
4	CATHODIC SWEEP FOR $ZnO \cdot Co$ ELECTRODE IN 8.8m KOH AND ZINCATE -----	27
5	CATHODIC SWEEP FOR A $ZnO \cdot Al$ ELECTRODE IN 8.8m + ZINCATE -----	28
6	CATHODIC SWEEP FOR $ZnO \cdot La$ ELECTRODE IN 8.8m KOH + ZINCATE -----	29
7	CATHODIC VOLTAMMOGRAM FOR PARTIALLY CHARGED ELECTRODE OF ACTIVATED ZnO DOPED WITH Pb & Cd --	30

SUMMARY

During this year's work, activated ZnO samples have been formulated which singly, or in combination with dilute electrolyte formulations, result in partially insoluble discharge products. Activated ZnO, prepared by alloy vaporization or by thermally accelerated diffusion of metallic dopants into the ZnO lattice, which had proved to be less soluble than pure ZnO, also proved to be less electrochemically active. This resulted, generally, in reduced efficiency, higher degrees of polarization and passivation and decreased conductivity. These properties are known to be detrimental to the performance of secondary Ni-Zn batteries and this approach was abandoned.

For this reason a new approach to electrode material formulation was adopted. Active material was mixed dry with materials which would provide an insoluble matrix after initial reaction in the cell electrolyte. These electrodes are expected to exhibit improved performance in two ways. Firstly, there is an even distribution of permanent, highly conductive nucleation sites along the apparent electrode surface, providing for even Zn deposition and distribution during charging. Secondly, the increase in effective surface area decreases actual current densities, thereby, decreasing overvoltages. This should decrease dendrite formation and gas evolution in addition to allowing for the use of higher apparent current densities.

Problems posed by the development of this type of electrode material are, for the most part, material selection problems. Materials must be chosen carefully, not just to fulfill their

ENERGY RESEARCH CORPORATION

given function within the electrode system, but also to provide for minimal counter-productive interaction with each other. Electrochemical evaluations of these types of materials show generally favorable behavior.

1.0 INTRODUCTION

One of the major drawbacks of the zinc anode in secondary batteries is the decay of cell capacity with cycling, which has been attributed to electrode shape change, passivation and dendritic growth. These problems may be traced to the solubility of the Zn anode in the cell electrolyte, changes in nucleation site distribution and subsequent complications such as potential and concentration gradients, mass transfer effects and electrolyte inventory problems.

The objective of this program is to investigate the partially insoluble Zn electrode as an approach to solving the aforementioned problems of the Zn electrode.

The major tasks of the program consist of preparation of activated or partially insoluble zinc oxides, determination of solubility of prepared materials in aqueous KOH solutions, electrochemical evaluation of promising formulations and full-scale cell testing of such materials.

2.0 TECHNICAL DISCUSSION

2.1 PREPARATION OF EXPERIMENTAL MATERIALS

It is believed that the performance of Zn anodes in secondary batteries depends on the nature and type of ZnO used in the fabrication of the anode. ZnO prepared utilizing the "French Process" is preferred to that prepared from the "American Process". The differences between these two types of ZnO may be attributed to variation in three basic properties of ZnO. These are semiconduction, sinter formation, and chemisorption. Of these properties, electronic conductivity has the largest influence on battery performance, particularly its variation with repetitive oxidation and reduction in a battery. Pure ZnO carefully prepared in the laboratory is an insulator. However, its conductivity can be altered by several orders of magnitude upon the introduction of specific impurities into the crystal lattice. ERC has adopted two methods for preparation of activated zinc oxides.

The first method is one which employs thermally accelerated diffusion of metallic dopants into the ZnO lattice. Dry ZnO is thoroughly mixed with a nitrate salt solution of the dopant. The mixture is air dried and then heated in a reducing atmosphere at 900°C for 15 minutes. The resulting product is ground to a fine powder.

The second method of preparation consists of first making an alloy of Zn and the dopant metal using the binary phase diagram as a guide. The alloy is then vaporized in an electric arc furnace using a proprietary procedure. The condensed vapors are collected in a series of bags corresponding to fractions of different particle size.

Another approach to the solution of the solubility problems of ZnO in secondary batteries is to create an insoluble, highly conductive substrate matrix containing permanent nucleation sites. Although this does not reduce the actual solubility of the ZnO, it does reduce the apparent solubility of the electrode. It also increases the apparent conductivity without altering the kinetic properties of ZnO.

This type of electrode material consists simply of a dry mix of ZnO, a material which forms an insoluble solid matrix upon hydration, a metallic oxide which reduces to an inert metallic state at the Zn/ZnO potential during initial charging of the battery, and a finely powdered, highly conductive metallic component.

Activated ZnO samples containing Fe, Co, Ni, Sn, Al, La and In were prepared using the thermally accelerated diffusion procedure. The alloy vaporization procedure was used to prepare activated ZnO samples containing Bi, Fe, Cd, Ce and Pb both singly and in combinations. Dry mixed materials were prepared, all containing ZnO, PbO, and Cu powder in combination with either Ca, Ba, Sr or a combination of Ca and Mg.

2.2 SOLUBILITY DETERMINATIONS

The solubility of experimentally prepared electrode materials in aqueous KOH solutions was determined. The procedure involves suspending the solutes in KOH solution and agitating the solution for 24 hours using a magnetic stirrer. The amount of Zn dissolved into solution is determined by either E.D.T.A. titration or atomic absorption analysis. This method was also used to determine the solubility of commercially available Zn salts. The results

are illustrated in Table 1. All of these compounds are capable of functioning as the major active material for a reversible Zn electrode.

The least soluble materials overall are zinc titanate and zinc fluoride. These materials were tested in 20 Ahr Ni-Zn batteries. Of the specially prepared materials, ZnO doped with Ce, Co, Cd and Sn exhibited the least solubility with respect to Zn. 20 Ahr batteries using ZnO doped with Ce and ZnO doped with Cd as active anode materials, were built and tested.

The effect of KOH concentration on solubility was determined for pure ZnO and activated zinc oxides containing Co and Sn. The data are summarized in Table 2. The solubility of Zn is seen to decrease with decreasing KOH concentration as expected. A KOH concentration of 20% has excellent potential as a cell electrolyte in view of favorable ZnO solubility, conductivity and freezing point.

2.3 EXPERIMENTAL EQUIPMENT

The experimental arrangement consists of an electrochemical cell, a constant temperature water bath, a P.A.R. potentiostat externally modulated by a P.A.R. Universal programmer and an x-y recorder. The electrochemical cell, see Figure 1, consists of a flat bottomed glass jar inside of which is arranged a second container made of polyethylene which contains the cell components and electrolyte. The cell was designed to be operated using about 0.5 liters of electrolyte saturated with ZnO. A plexiglass cover which seals both the polyethylene and glass containers is provided with inlet ports for working and counter electrode leads and the reference electrode Luggin capillary.

The cell was airtight and was purged with dried nitrogen gas prior to use, in an effort to minimize carbonation of the electrolyte and to provide agitation of the electrolyte.

Counter electrodes were fabricated from fine Ni screen and formed to a semi-cylindrical shape. The actual surface area of the counter electrodes was approximately 500 cm².

The working electrodes are disc shaped, with an apparent surface area of 0.9989 cm². They are fabricated by roll-bonding a homogenous mixture consisting of 98% experimental active material and 2% TFE. The material is then cut to size and pressed onto an Ag current collector, using about 5 tons of applied pressure. The collector consists of a circular substrate of 35 mesh Ag expanded metal screen spot-welded to a 0.002 inch thick Ag foil disk. The entire electrode assembly is held in a high density Teflon fixture designed to allow maximum diffusion.

Working electrode potentials were monitored using a Hg/HgO reference electrode with a liquid junction, equipped with a Luggin capillary probe. The top of the probe sits less than 1 mm from the electrode surface. As different electrolyte concentrations were used in the cell, the electrolyte in the reference electrode was changed to minimize possible junction potential errors.

2.4 ELECTROCHEMICAL EVALUATIONS

2.4.1 Efficiency Tests

There are two efficiency tests, one at an electrode utilization level of 17% and one at 100% theoretical electrode utilization. The two tests differ only in the amount of cathodic charge to which

the electrode is subjected, relative to its theoretical capacity.

In both tests, the electrodes are charged to the specified utilization level, relative to their theoretical capacity at a constant current density equivalent to that used in standard Ni-Zn batteries which is approximately $4 \text{ mA}\cdot\text{cm}^{-2}$.

After cathodic charging the electrode is allowed to equilibrate for about 1 hour or until a stable equilibrium potential is achieved. The electrode is then discharged at a constant current density of approximately $10 \text{ mA}\cdot\text{cm}^{-2}$ while E (vs. Hg/HgO) vs. time is recorded. The quantity of charge output is then calculated using 1.00 Volt vs. Hg/HgO as the cutoff potential. The coulombic efficiency is taken as the anodic charge output over the cathodic charge input (Q_a/Q_c).

Electrochemical solubility is determined by comparing Zn^{2+} concentration in the electrolytes employed in the efficiency tests, with that in freshly prepared electrolyte. An increase in Zn^{2+} concentration with testing gives a positive value for electrochemical solubility and indicates that a larger amount of Zn than was deposited from the electrolyte during charge, was dissolved during discharge. A decrease in Zn^{2+} concentration with testing gives a negative value for electrochemical solubility, indicating that dissolution of Zn during charge, was inhibited during discharge.

Efficiency and electrochemical solubility data for some of the experimental electrode materials is given in Table 3. The data for pure ZnO are also presented for comparison. Note that for pure ZnO in 8.8m KOH solution with zincate, the efficiency exceeds 100%. This is due to deposition of Zn from the electro-

ENERGY RESEARCH CORPORATION

lyte upon charge and subsequent dissolution upon discharge.

Note also the efficiency values, taken from tests in 8.8m KOH with zincate, at charge input levels of 100% of theoretical capacity. All of the materials exhibited efficiencies of about 70-90%. These values represent a maximum obtainable coulombic efficiency for the ZnO electrode in KOH electrolytes at full electrode utilization. At a KOH concentration of 8.8m dopants and additives appear to have little effect on efficiency and electrochemical solubility. It is thought that the corrosive effects of KOH electrolyte at this concentration tend to disrupt the structure of these altered zinc oxides. This was a contributing factor in the choice of 4.2m KOH solution with zincate at the optimum electrolyte formulation.

Electrochemical solubility for LBL-019 and LBL-014, unlike the chemical solubility is generally larger than that for pure ZnO. The efficiency values for these materials, although still less than the corresponding values for pure ZnO, are generally larger than those of the other experimental materials. Apparently decreased ionic activity is not always accompanied by a similar decrease in electronic activity. It is, however, electrochemical and not chemical solubility which is believed to be responsible for many problems associated with Zn anode failure in secondary batteries.

LBL-013 displays the least electrochemical solubility of all the materials tested including pure ZnO. Efficiency values, however, are also the lowest of all the materials tested. The decreased electronic activity responsible for good solubility characteristics is also responsible for unfavorable coulombic efficiency characteristics.

Page No. 9

Electrochemical solubility values for LBL-015 in 4.2m KOH are only slightly larger than those for pure ZnO and are accompanied by only slightly smaller efficiency values. In 1.95m KOH, the solubility drops below that given for pure ZnO. Unfortunately efficiency in this electrolyte also drops substantially below that of pure ZnO.

Of the experimental materials, LBL-015 in 4.2m KOH was judged to be the best compromise between electrochemical solubility and efficiency.

In general, the data seems to show that electrochemical solubility cannot be decreased without a resultant sacrifice in coulombic efficiency and that coulombic efficiency cannot be increased without a corresponding increase in electrochemical solubility and the problems which accompany it.

2.4.2 Cyclic Voltammetry

Electrodes containing the various experimental materials are subjected to about 100 potentiodynamic scans from -1.200V to -1.400V (vs Hg/HgO) at a sweep rate of 2mV Sec⁻¹. Current-potential profiles are recorded for each of the first five to ten scans, and every fifth scan thereafter. Often, due to intrinsic properties of the electrode material, the anodic and/or cathodic reactions do not occur to any significant extent, within the specified potential range, necessitating a slight alteration of the potential range in order to obtain useful data. An effort is always made to keep the potential range such that the effects of H₂ evolution are kept to a minimum.

As in the efficiency tests, none of the experimental materials performed as well in cyclic voltammetry tests as did pure ZnO. All of the materials tested were shown to be more polarizable than pure ZnO and all but two electrolyte-experimental material combinations were shown to be less reactive than pure ZnO, as evidenced by smaller peak current values. This type of behavior is indicative of increased Ohmic resistance in the experimental materials as compared to pure ZnO.

Both LBL-014 and LBL-017 exhibited larger peak anodic currents than pure ZnO in 8.8m. KOH solution with zincate. This appears, however, to be due to differences between the state of charge of the experimental materials, and that of the ZnO electrode, rather than to increased reactivity of the experimental materials. This speculation has been confirmed by further testing of these materials.

Other curious behavior was also observed from these two materials in cyclic voltammetry tests. LBL-014 did not show any signs of decay in performance when tested in 4.2m KOH solution but instead showed a steady improvement in performance with cycling. Initial performance, however, was poor and LBL-014 did not achieve peak currents equivalent to those of pure ZnO until about the 25th cycle, when pure ZnO performance had already deteriorated substantially. Performance in 8.8m KOH electrolyte showed very little decay in performance, although initial performance was poor. Performance in 1.95m KOH electrolyte was very poor; the peak anodic and cathodic current values decreased

steadily with cycling from the very first cycle. This result indicates progressive passivation of the electrode with cycling. The reversible potential in all electrolytes was 10-20 mV more cathodic than that for pure ZnO.

LBL-017 exhibited very encouraging performance in 4.2m KOH electrolyte. Peak currents were almost as large as those for pure ZnO and faradaic efficiency did not begin to decay until the 11th cycle, only two cycles sooner than for pure ZnO. Performance in 8.8m KOH electrolyte was only slightly better than in 4.2m KOH electrolyte, while performance in 1.95m KOH electrolyte was very poor and showed evidence of large Ohmic resistances in that electrolyte. Reversible potential values were about 25 mV more cathodic than those for pure ZnO.

LBL-009 ($\text{Zn}_x\text{Co}_{0.04x}\text{O}$) despite encouraging solubility characteristics performed very poorly in all electrolyte concentrations. It was shown to be extremely polarizable and evolved H_2 gas at lower over potentials than those at which Zn^{2+} reduction occurred. Reversible potential values were about 500 mV more anodic than those for pure ZnO.

LBL-003 and LBL-013 both exhibited fair performance in concentrated electrolyte but displayed rapid deterioration of performance as electrolyte concentration was decreased.

Performance similar to that of pure ZnO was seen from LBL-015 with the exception that peak current density values were slightly smaller for the experimental material.

LBL-019 exhibited an i-E profile unlike any of the other experimental materials. Numerous anodic current peaks were observed in addition to the one associated with

Zn oxidation. These other reactions are assumed to be oxidation reactions of the various electrode components present in addition to ZnO. The Zn reaction was more polarizable than that occurring on a pure ZnO electrode in all electrolyte concentrations. Reversible potentials in all electrolytes were about 40 mV more anodic than those for pure ZnO.

Some of the cyclic voltammograms in 4.2 m and 1.95 m KOH exhibited small capacitive discharge peaks. This behavior was independent of the material being tested. It is speculated that these peaks may be due to the formation of a highly resistive oxide film on the electrode surface via a corrosion reaction.

2.4.3 Cathodic Polarization Studies

The experimental electrodes are galvanostatically charged at $3.5 \text{ mA} \cdot \text{cm}^{-2}$ to 90% of their theoretical capacity resulting in electrodes in which the Zn:ZnO ratio is 9:1. After charging, each electrode is allowed to relax until a stable equilibrium state is achieved. It is then subjected to potentiodynamic scanning in the direction of increasing cathodic potential from the approximate equilibrium (OCV) potential to about -1.65V vs Hg/HgO. The electrode is then allowed to relax for about the same amount of time as was consumed by the scanning process, before being subjected to the same process again. Current-potential curves for each scan are recorded. This is repeated about twenty times depending on the resolution and clarity of the i-E curves obtained.

Cathodic polarization studies were very informative as they provided information about the H_2 evolution reactions as well as the Zn^{2+} reduction reactions. Pure ZnO performed rather poorly in this test. H_2 evolution began to occur almost immediately after Zn^{2+} reduction and increased rapidly as potential became more cathodic. Peak Zn^{2+} reduction current densities occurred at 1.41V vs Hg/HgO in 1.95M KOH electrolyte. LBL-003 performed similarly with the Zn^{2+} reduction peak occurring at 1.48V vs. Hg/HgO. However, H_2 evolution did not occur until the electrode potential reached 1.53V vs. Hg/HgO. It did not increase quite as rapidly as the electrode of pure ZnO.

LBL-009 displayed dismal performance due to an overlap in the potential regions of both the Zn^{2+} reduction and H_2 evolution reactions. Performance of LBL-013 was more encouraging. Zn^{2+} reduction current density values were approximately double those of pure ZnO and LBL-003, with peak values occurring at 1.52V vs. Hg/HgO in concentrated electrolytes. H_2 evolution current densities were smaller than those of the previously mentioned materials and did not increase quite as rapidly with increasing overpotential.

H_2 evolution current densities exhibited by LBL-014 were generally much larger than peak Zn^{2+} reduction current densities and both were much larger than any current densities exhibited by any other materials in this test.

The most encouraging performance in these tests was exhibited by LBL-015, LBL-017 and LBL-019. These materials all showed minimal H_2 evolution in combination with substantial

Zn^{2+} reduction occurring at 1.43V vs. Hg/HgO in 4.2M KOH electrolyte. The corresponding potential values for LBL-019 was the same but was accompanied by smaller current density values. LBL-015 exhibited Zn^{2+} reduction peak currents at 1.46V vs. Hg/HgO in 4.2M KOH electrolyte. The H_2 evolution behavior of this material was notable in that H_2 evolution currents decreased with increasing overpotential.

2.5 CELL TESTS

The most promising experimental materials were chosen for testing in standard configuration 20 Ahr Ni-Zn secondary batteries. Cathodes were roll bonded ERC $\text{Ni}(\text{OH})_2$ electrodes. Prior to regular cycling, each cell was subjected to 2-6 "formation cycles", in which the cell was charged to 160% of its full rated theoretical capacity and then discharged at a C/2 rate. This process fully activates the nickel electrode material. Regular cycling consists of a six hour charge at a current density of $4 \text{ mA}\cdot\text{cm}^{-2}$ and subsequent discharge at a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ to a cell potential of 1.25V.

Zinc borate, zinc fluoride and zinc titanate were tested as additives to a standard ZnO electrode. The additive concentration in these electrodes was 10%. The cells never delivered more than 19Ahr and showed stable capacity performance for only 17 cycles in the best case. The best cell containing zinc fluoride only gave 26 cycles delivering between 17 and 20 Ahr. Cells containing zinc titanate gave an average of 36 cycles, delivering between 17 and 20 Ahr.

Anode shape change and subsequent problems were the cause of failure in all cases.

Single anode prototype cells were also built using zinc fluoride, zinc borate or zinc titanate as the exclusive active material in the anode. The nominal theoretical capacity of these cells was 3.3 Ahr. The zinc borate cell was only capable of delivering 1.0 Ahr of discharge capacity while the zinc fluoride cell only delivered 0.8 Ahr. The zinc titanate cell gave no discharge capacity whatsoever. Apparently zinc titanate is very polarizable and incapable of storing charge.

Standard Ni-Zn cells were built using LBL-100 as the active anode material. These cells performed poorly delivering less than 15 Ahr of discharge capacity. The suspected reasons for poor performance are poor electrode structural integrity and subsequent poor collector to electrode bonding. These phenomena were observed prior to assembly of the cells.

Two of the new type of experimental materials were also tested in standard 20 Ahr cells, LBL-015 and LBL-019. Both materials performed similarly. None of the cells were capable of delivering more 12 Ahr, even after charging to 160% of theoretical capacity. Half cell potentials during discharge and post operative examination revealed failure to be due to contamination of the Ni(OH)_2 cathode by components of the anode. This occurs as soluble components of the anode precipitate at the surface of the cathode, causing it to become extremely polarizable and incapable of storing a charge.

ENERGY RESEARCH CORPORATION

More encouraging data has recently been obtained from cells built using formulations LBL-160, LBL-170 and LBL-180 which are also based on the insoluble, conductive matrix concept. Composition of these materials is given in Table 4. These three materials performed very similarly. Although these cells never delivered more than 19 Ahr, performance has been extremely stable up to 47 cycles with the average cell capacity for each formulation being about 17.5 Ahr at the 47th cycle. Cycle testing of these cells is continuing until capacity decays to 12 Ahr, which represents 60% of the nominal capacity of these cells.

3.0 CONCLUSIONS

The electrochemical properties of the ZnO lattice can be altered via insertion of metallic dopents making it less soluble. Decreased solubility, however, especially electrochemical solubility also results in a decrease of other types of electrochemical activity, which in turn cause low efficiency and conductivity and increased polarizability. These effects make this an unacceptable approach for the formulation of exclusive anode materials, although use of such formulations as additives may be helpful in combating counter productive hydrogen evolution.

A more workable approach has been found in the use of pure ZnO in conjunction with other materials which after initial hydration and charging form a highly conductive and insoluble matrix. This matrix provides increased actual surface area and an evenly distributed network of permanent nucleation sites for Zn deposition.

Full scale cell tests of some of these anode materials have shown them to form substantially more stable anodes than pure ZnO alone. Performance decay with the repetitive oxidation and reduction of secondary battery cycling has been shown to be minimal.

TABLE 1
SOLUBILITY DATA

Material/#	Composition	Solub.in 35% KOH mg Zn/ml solution	Moles Zn	Method of Preparation
Zinc Oxide	Pure ZnO (USP-19)	68.2899	1.0447	Commercially Available
Zinc Fluoride	$\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$	1.6168	0.0247	"
Zinc Borate	$\text{Zn}_2\text{B}_6\text{O}_{11}$	8.7378	0.1337	"
Zinc Ferrite	ZnFe_2O_4	26.8271	0.4104	"
Zinc Titanate	ZnTiO_3	3.8786	0.0593	"
Zinc Cyanide	$\text{Zn}(\text{CN})_2$	77.79	1.190	"
LBL-100	ZnO	70.70	1.082	Alloy Vapor- ization
LBL-200	$\text{ZnO}+0.9\%\text{Bi}$	66.40	1.016	"
LBL-300	$\text{ZnO}+4.8\%\text{Cd}$	62.90	0.9622	"
LBL-400	$\text{ZnO}+10\%\text{Cd}$	56.80	0.8689	"
LBL-500	$\text{ZnO}+1.3\%\text{Fe}$	75.75	1.159	"
LBL-011	$\text{ZnO}+0.15\%\text{Ce}$	47.50	0.7266	"
LBL-012	$\text{ZnO}+8.7\%\text{Pb}$	56.60	0.8658	"
LBL-001	ZnO	68.02	1.040	Thermally Accelerated Diffusion
LBL-002	ZnFe_2O_4	68.19	1.043	"
LBL-003	$\text{Zn}_x\text{Sn}_{0.006x}\text{O}_x$	60.59	0.9269	"
LBL-004	$\text{Zn}_x\text{Ni}_{0.006x}\text{O}_x$	69.90	1.069	"
LBL-005	$\text{Zn}_x\text{Fe}_{0.006x}\text{O}_x$	73.24	1.120	"
LBL-006	$\text{Zn}_x\text{Co}_{0.006x}\text{O}_x$	55.10	0.8429	"
LBL-007	$\text{Zn}_x\text{In}_{0.006x}\text{O}_x$	69.29	1.060	"
LBL-008	$\text{Zn}_x\text{Co}_{0.004x}\text{O}_x$	68.31	1.045	"
LBL-009	$\text{Zn}_x\text{Co}_{0.04x}\text{O}_x$	64.0	0.979	"
LBL-010	$\text{Zn}_x\text{Sn}_{0.02x}\text{O}_x$	58.8	0.899	"
LBL-013	$\text{Zn}_x\text{Al}_{0.006x}\text{O}_x$	60.66	0.9279	"
LBL-014	$\text{Zn}_x\text{La}_{0.006x}\text{O}_x$	59.23	0.9061	"

TABLE 2
EFFECT OF KOH CONCENTRATION
ON THE SOLUBILITY OF DOPED ZnO

SOLUBILITY ~ mg/ml (as ZnO)						
Wt. % KOH	PURE ZnO	ZnO+Sn (003)	ZnO+Co (009)	ZnO+La (014)	ZnO+PB (017)	CaZnO ₂
45	135	129	125	101	98	107
35	85	73	61	59	71	66
30	66	43	47	-	-	53
20	33	18	20	21	57	16
15	16	9	9	-	-	-
10	7	5	8	9	5	-

TABLE 3
EFFICIENCY AND ELECTROCHEMICAL SOLUBILITY DATA

ELECT.MAT'L	ELECTROLYTE	ELECT.UTIL. CHG Input/ Theo.Cap.)	COULOMBIC EFFIC. (%)	ELECTCHEM. SOLUB. (4Zn)
Pure ZnO (USP Grade 19)	1.95M KOH+	0.17	85.27	2.59×10^{-3}
	0.007M Zn ²⁺	1.00	80.67	5.25×10^{-3}
	in aq.sol'n			
	4.2M KOH+	0.17	80.24	-2.37×10^{-2}
	0.07M Zn ²⁺	1.00	80.35	-2.03×10^{-2}
	in aq.sol'n			
	8.8M KOH+	0.17	103.74	2.26×10^{-2}
	0.2M Zn ²⁺	1.00	86.64	-1.28×10^{-2}
LBL-014 (Zn _x La _{0.006x} O _x)	1.95M KOH+	0.17	61.49	-1.64×10^{-2}
	0.017M Zn ²⁺	1.00	44.28	---
	in aq.sol'n			
	4.2M KOH+	0.17	80.66	5.77×10^{-3}
	0.07M Zn ²⁺	1.00	85.12	8.08×10^{-3}
	in aq.sol'n			
	8.8M KOH+	0.17	85.81	8.64×10^{-2}
	0.2M Zn ²⁺	1.00	84.90	5.74×10^{-2}
LBL-013 (Zn _x Al _{0.006x} O _x)	1.95M KOH+	0.17	30.29	---
	0.017M Zn ²⁺	1.00	63.02	-1.13×10^{-2}
	in aq.sol'n			
	4.2M KOH+	0.17	46.11	-2.92×10^{-2}
	0.07M Zn ²⁺	1.00	61.09	-2.33×10^{-2}
	in aq.sol'n			
	8.8M KOH+	0.17	65.62	---
	0.2M Zn ²⁺	1.00	77.57	-4.59×10^{-3}
LBL-15 (See Table 1)	1.95M KOH+	0.17	50.22	-2.58×10^{-2}
	0.01M Zn ²⁺	1.00	53.74	-2.91×10^{-2}
	in aq.sol'n			
	4.2M KOH+	0.17	75.69	-1.72×10^{-2}
	0.07M Zn ²⁺	1.00	83.48	-2.41×10^{-2}
	in aq.sol'n			
	8.8M KOH+	0.17	83.78	3.0×10^{-3}
	0.2M Zn ²⁺	1.00	78.00	-1.4×10^{-3}
LBL-019 (See Table 1)	1.95M KOH+	1.00	77.93	5.06×10^{-3}
	0.017M Zn ²⁺			
	in aq.sol'n			
	4.2M KOH+	1.00	85.61	5.90×10^{-3}
	0.07M Zn ²⁺			
	in aq.sol'n			
	8.8M KOH+	1.00	74.17	-133×10^{-2}
	0.2M Zn ²⁺			
	in aq.sol'n			

TABLE 4

NEW ZNO COMPOUNDS UNDER STUDY

#	% ZNO	% PbO	% Cu	% TFE	ADDITIVE & %	OTHER TREATMENT
LBL-015	54.0	0	6.0	2.0	CA(OH) ₂ 38%	NONE
LBL-019	48.0	8.0	2.0	2.0	BA(OH) ₂ 40%	NONE
LBL-020	"	"	"	"	"	SINTERED
LBL-021	"	"	"	"	SR(OH) ₂ 40%	NONE
LBL-022	"	"	"	"	"	SINTERED
LBL-023	"	"	"	"	CA(OH) ₂ 30% MgCO ₃ 10%	NONE
LBL-024	"	"	"	"	"	SINTERED

TABLE 5
ADDITIONAL ZnO COMPOUNDS UNDER STUDY

LBL-160	52% ZnO 28% Ca(OH) ₂ 10% Zn powder 5% CdO 5% Bi ₂ O ₃
LBL-170	52% ZnO 28% Ca(OH) ₂ 10% Zn powder 5% CdO 5% Ga ₂ O ₃
LBL-180	52% ZnO 28% Ca(OH) ₂ 10% Zn powder 5% CdO 5% PbO
LBL-190	52% ZnO 28% Ba(OH) ₂ 10% Zn powder 5% CdO 5% Bi ₂ O ₃

POLARIZATION CELL

FIGURE 1

CYCLIC VOLTAMMOGRAM
IN 1.95 M. KOH+Zn²⁺ CYCLE #25

FIGURE 2

CYCLIC VOLTAMMOGRAM IN
8.8 M. KOH CYCLE #25

FIGURE 3

CATHODIC SWEEP FOR $\text{ZnO}\cdot\text{Co}$ ELECTRODE IN 8.8M KOH AND ZINCATE. PEAK A CORRESPONDS TO ZN REDUCTION.

FIGURE 4

CATHODIC SWEEP FOR A $\text{ZnO} \cdot \text{Al}$ ELECTRODE
IN 8.8M KOH + ZINCATE. PEAK A
CORRESPONDS TO ZnO REDUCTION.

FIGURE 5

CATHODIC SWEEP FOR ZnO·LA ELECTRODE IN 8.8M KOH + ZINCATE. PEAK A CORRESPONDS TO ZnO REDUCTION.

FIGURE 6

CATHODIC VOLTAMMOGRAM FOR PARTIALLY CHARGED ELECTRODE OF ACTIVATED ZnO DOPED WITH Pb & Cd . THE ELECTROLYTE IS 4.2 KOH AND 0.07M Zn^{2+} IN AQUEOUS SOLUTION.

FIGURE 7

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

7 3-12-68

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720

100