A NOVEL HIGH POWER AND ENERGY DENSITY ENVIRONMENTALLY COMPATIBLE ALUMINUM/PERMANGANATE BATTERY

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The search for contemporary batteries with the requisite high power and energy densities for electric propulsion of vehicles has blurred the conventional distinctions of electrochemical storage systems, and no available system is considered satisfactory. Candidates include mechanically rechargeable primary batteries, secondary batteries and fuel cells (1-9). Nonaqueous systems are being actively developed[2-7], but challenges of environmental compatibility, conductivity, cost, safety or power density remain and aqueous systems dominate both the consumer and electric propulsion market (1). There have been few new high capacity aqueous batteries introduced. Aqueous batteries utilizing metal hydride or air cathodes are being actively developed, and challenges including cost, CO_2 poisoning and power densities are being addressed (7-9).

An environmentally compatible novel aqueous aluminum/permanganate battery is discussed with the potential for unusually high pulsed power densities and with high theoretical sustained specific energy.

Conventional nickel/cadmium and lead acid batteries have moderate to low energy densities and adverse environmental impact. As seen in Table I, zinc/silver oxide batteries have a higher theoretical energy capacity, however the silver oxide cathode is not cost effective for large scale systems (7).

Compared to zinc cells, aluminum cells can yield substantially higher energy capacities. The theoretical potential of an aluminum anode is greater than one volt more favorable than the zinc anode potential. Furthermore, the theoretical storage capacity of Al (2980 A hr/kg) is substantially higher than that of zinc (820 A hr/kg). As seen in Table I, these combined characteristics lead to a three fold higher energy capacity for aluminum compared to zinc/silver oxide batteries. Aluminum/silver oxide batteries have among the highest measured steady

state power densities, and are useful for the requisite high discharge rates necessary for electrochemical propulsion (7, 12). However the high cost of silver is an impediment to the use of aluminum/silver oxide cells for land-based electric vehicle propulsion.

Aluminum is among the most common elements, and its light weight, electronegative potential and three electron oxidation state make it a compelling anode material (9). Electronegative anodes such as aluminum might be considered incompatible (reactive) when immersed in a strong oxidizing agent. However, this problem is circumvented by utilizing the extraordinarily high oxidative currents accessible for aluminum in aqueous alkaline media (10,11). We recently used a model system with a ferricyanide cathode to demonstrate that such aluminum batteries are possible when the redox phase cathode can also support high current densities (10). The Al/ferricyanide demonstrated high power densities (in excess of $2W/cm^2$ over simple planar surfaces). Al/ferricyanide has a modest specific energy (96 Wh/kg) which can be theoretically exceeded by an alternative aluminum/permanganate cell (Table I). A permanganate cell operating in a manner similar to the Al/ferricyanide cell may also provide high power densities.

(Mn(IV)) has found wide spread, cost effective use in Leclanché and alkaline batteries and does not pose the environmental threat of cadmium or lead in batteries (7). Permanganate (Mn(IV)), MnO_4^-, has a more attractive cathodic potential and storage capacity than MnO_2.

The new battery is expressed by aluminum oxidation and permanganate reduction:

anode: $Al + 4OH^- \rightarrow Al(OH)_4^- + H_2O + 3e^-$
$-E^o = -2.3$ V vs SHE

cathode: $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$
$E^o = 0.6$ V vs SHE

discharge: $Al + MnO_4^- + 2H_2O \rightarrow Al(OH)_4^- + MnO_2$
$E_{cell} = 2.9$ V

Based on lithium, sodium or potassium salts this represents high theoretical specific energies respectively of 1230, 1140 and 1070 Wh/kg. A comparison of the capacities of aluminum/permanganate and existing cells including our recent aluminum/sulfur battery (13) is provided in Table I accentuating the theoretical advantage of the permanganate cell.

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Table I. Conventional and new high energy density aqueous batteries.

System	Cell Potential, OCV Theoretical	Observed	Charge Capacity*	Maximum* Energy Density
Lead Acid	2.04 V	2.0 V	83 Ahr/kg	174 Whr/kg
Nickel/Cadmium	1.35 V	1.2 V	181 Ahr/kg	244 Whr/kg
Zinc/Silver Oxide	1.57 V	1.4 V	199 Ahr/kg	312 Whr/kg
Aluminum/Silver Oxide	2.69 V	2.0 V	378 Ahr/kg	1020 Whr/kg
Aluminum/Ferricyanide	2.8 V	2.2 V	81 Ahr/kg	227 Whr/kg
Aluminum/Sulfur	1.8 V	1.4 V	595 Ahr/kg	1070 Whr/kg
Aluminum/Permanganate	2.9 V	2.3 V	476 Ahr/kg	1380 Whr/kg

*Theoretical, per kg stored reactant, assumes water activated cell in a H_2SO_4 or sodium (hydroxide) electrolyte