Determination of $Ag^{I}Cu^{III}O_2$ Discharge Mechanism

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The energy density of the silver oxide cathode is among the highest of all aqueous battery cathodes.[1] Silver oxide is best known as an alkaline cathode coupled with zinc, and has found niche consumer applications in small devices requiring high energy density. The two major short-comings of the silver oxide/zinc system are dendrite formation due to the partial solubility of the divalent and monovalent forms of silver oxide and the high cost of silver.[1] Although improvements in membrane technology have greatly increased the storage lifetime of silver oxide/zinc cells by decreasing silver migration to the anode compartment, attempts to produce a low cost high energy density analog of silver oxide have been far less successful.[2,3,4]

A number of alternative silver cathodes which contain less silver per formula unit have been developed. Materials such as $AgNiO_2$, $Ag_5Pb_2O_6$ and $AgBiO_3$ all contain less silver, but sacrifice some capacity as a result of their electrochemically inactive substituents.[2,3,4] Recently, $Ag^{I}Cu^{III}O_2$ and $Ag_2^{I}Cu_2^{II}O_3$ have been uncovered in the Ag-Cu-O ternary system.[5-10] Unlike other trivalent copper compounds such as $NaCu^{III}O_2$ and $KCu^{III}O_2$, $AgCuO_2$ has been reported to be insensitive to moisture and stable in air for months. The trivalent copper compound $AgCuO_2$ forms a two-dimensional layered Delafossite structure with an interlayer spacing of 6 Å and has a density of 7.1 g/cc. Comparatively, the divalent copper compound, $Ag_2Cu_2O_3$, is isostructural and isoelectronic with the mineral Paramelaconite, Cu_4O_3, and forms a three dimensional crystal structure.

Herein, the electrochemistry of the trivalent copper compound $AgCuO_2$ in alkaline electrolyte is presented for the first time. The alkaline discharge mechanism of $Ag^{I}Cu^{III}O_2$ is characterized at room temperature using linear sweep voltammetry (Figure 1) and ex-situ x-ray powder diffraction (Figure 2). Four distinct discharge processes are resolved at +0.35, +0.06, -0.28 and -0.56 V (vs. Hg/HgO). A discharge mechanism:

$2AgCuO_2 + H_2O + 2e^- \rightarrow Ag_2Cu_2O_3 + 2OH^-$ +0.35 V
$Ag_2Cu_2O_3 + H_2O + 2e^- \rightarrow 2Ag^o + 2CuO + 2OH^-$ +0.06 V
$2CuO + H_2O + 2e^- \rightarrow Cu_2O + 2OH^-$ -0.28 V
$Cu_2O + H_2O + 2e^- \rightarrow 2Cu^o + 2OH^-$ -0.56 V
$2AgCuO_2 + 4H_2O + 8e^- \rightarrow 2Ag^o + 2Cu^o + 8OH^-$

is proposed based upon analysis of ex-situ x-ray powder diffraction patterns of the discharge products.

$AgCuO_2$ has also been evaluated as a non-aqueous cathode against a lithium anode. Preliminary results show that the $AgCuO_2$ cathode has a relatively low average running voltage (1.5-2.0 V) with respect to lithium. Specific capacities of 393 and 296 mAh/g at a 1.5 V cut-off were obtained in stage cells under low (I = 10 mA/g) and high (I = 100 mA/g) discharge rates, respectively.

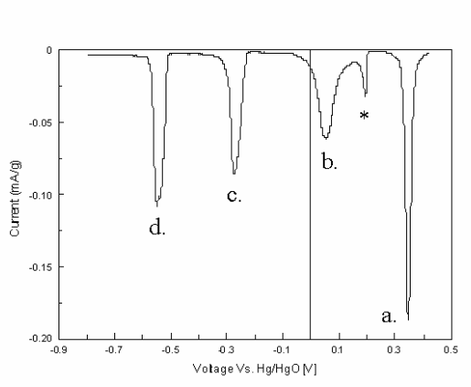

Figure 1: Linear sweep voltammogram of $AgCuO_2$, collected using sweep rate = 0.01 mV/sec. Four major discharge processes are observed at a. +0.35 V, b. +0.06 V, c. -0.28 V and d. -0.56 V. Discharge process at +0.18 V, denoted *, corresponds to Ag_2O impurity. Voltages reported with respect to Hg/HgO reference electrode.

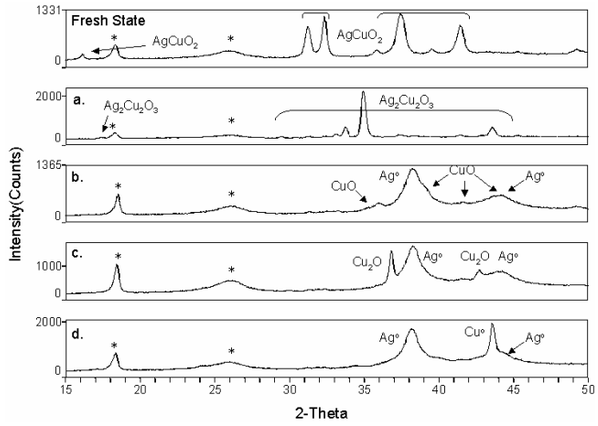

Figure 2: Ex-situ x-ray powder diffraction patterns of $AgCuO_2$ cathode mixtures, corresponding to the discharge products from discharge processes a., b., c. and d. shown in Figure 1. Teflonized acetylene black denoted with *.

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