STUDIES ON ALKALINE ZINC-AIR CELL EMPLOYING GELLED ELECTROLYTE

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ABSTRACT

A zinc-air air cell of monopolar design was fabricated employing a zinc metal foil as the anode, an aqueous potassium hydroxide (KOH) electrolyte and a thin air cathode sheet. The air cathode sheet consisted of laminated structures of fibrous carbon dispersed with a manganese catalyst and supported by a nickel mesh. A semi permeable hydrophobic Teflon membrane encapsulated the airside of the electrode. The cell components were enclosed in a home-made cylindrical plastic casing 28-mm in height and 45-mm in diameter. A commonly known hydroponics gel was introduced as a new electrolyte gelling agent for the alkaline zinc-air cell. Upon mixture with the aqueous KOH electrolyte, it expanded into loosely bound elastic jelly granules. The fabricated zinc-air cells were characterized according to their open circuit voltage (OCV), operating voltage as a function of galvanostatic discharge current, power density profile and discharge at constant current. The cell capacities obtained initially were comparatively low; 229, 165 and 115 mAh rated at 5, 50 and 100 mA, respectively. The Scanning Electron Microscopy (SEM) observations and the X-Ray Diffraction (XRD) analysis showed that the cell's failure was due to the formation of a zinc oxide insulating layer and not due to any side reactions between the gel and the electrode or the electrolyte. Zinc oxide is regarded as the end product of zinc-air cell chemistry. Presumably the low discharge capabilities of the cell were attributed to the low surface area of the planar zinc electrode, interfacial resistance due to the KOH electrolyte in the jelly-like forms and the limited amount of free KOH electrolyte available to the electrodes due to the higher water retentivity of the gel. A thin KOH-treated agar layer was introduced between the electrode-gelled electrolyte interfaces to improve the interfacial contact and serve as an electrolyte reservoir to the electrode. Agar is a natural biodegradable polymer extracted from marine algae with gel forming properties. The delivered zinc-air cell capacities were enhanced outstandingly to 711, 240 and 163 mAh at discharge current of 5, 50 and 100 mA, respectively. In order to further improve the cell performance, porous zinc electrodes were prepared from a zinc-graphite-agar paste. When dried the agar acted as a binder to the electrode structure. The graphite

content and the agar solution concentration were varied to find the best electrode composition. The inclusion of particulate graphite into the electrode did not enhance the electrode performance due to the formation of a graphite-rich layer, which obscured the electrode porosity. Above 5 mg cm^{-3} solution concentration, the dried agar formed a film that was thick enough to shield the zinc active material and thus reduced the cell capacity. Using the porous zinc electrode, the resulting cell capacities achieved were 1910 and 2066 mAh at rated current load of 0.1 A and 50 mA, respectively. The corresponding specific energy densities were 420 and 443 Wh kg^{-1} respectively. These performances at the rated current load could be regarded as comparable to present zinc-air batteries. A cyclic voltammetry study was performed on the zinc and air electrodes in gelled electrolyte to ascertain the effect of gelling using the hydroponics gel to the electrode kinetics. As anticipated the gelling caused considerable hindrance to the electrode kinetics due to the limited free electrolyte nature and the gel structure. These characteristics of the gelled electrolyte on the other hand, induced several interesting features of particular interest in the development of the secondary alkaline zinc battery. The solubility and mobility of the zinc oxidation product were reduced and hence improved the redeposition of the zincate species substantially. Both the oxygen and hydrogen evolution potentials were also attenuated as a consequence of using the gelled electrolyte. The structure of the fibrous carbon of the commercial air electrode was not suitable for use with the gelled electrode. It hindered the penetration of the gelled electrolyte and thus the large surface area was not fully utilized. For the zinc electrode, the application of the agar layer as the electrolyte reservoir eased the hindrance caused by the gelled electrolyte. As for the air electrode, the use of the agar layer was essentially useful in maintaining the wettability of the electrode throughout the cell operation.

ABSTRAK

Sel zink-udara berstruktur monopolar telah difabrikasi menggunakan foil logam zink sebagai anod, elektrolit akues kalium hidroksida (KOH) dan kepingan nipis katod udara. Kepingan katod udara ini terdiri daripada lapisan serabut karbon bersalut manganum yang berfungsi sebagai pemangkin dan strukturnya ditampung oleh kasa dawai nikel. Permukaan dedahan udara diselaputi membran Teflon separa telus yang bersifat anti-air (*hydrophobic*). Sebuah penakung plastik buatan sendiri, berbentuk selinder dan berdimensi 28 mm tinggi dan 45 mm diameter, digunapakai bagi menampung komponen-komponen sel tersebut. Gel hidroponik yang dikenali umum telah diperkenalkan sebagai agen penampung elektrolit bagi sel zink-udara beralkali. Apabila dicampurkan dengan elektrolit akues KOH, gel hidroponik akan mengembang kepada butir-butir jeli yang anjal. Sel-sel zink-udara yang telah siap difabrikasi dicirikan oleh voltan litar terbuka, voltan operasi berfungsikan arus keluaran yang malar, profil ketumpatan tenaga dan discas pada arus malar. Secara bandingannya kapasiti sel yang diperolehi adalah rendah; 229, 165 dan 115 mAh yang dicirikan pada arus keluaran malar 5, 50 mA dan 100 mA masing-masing. Pemerhatian daripada mikroskop elektron (SEM) dan kajian belauan sinar-X (XRD) menunjukkan penamatan hayat sel disebabkan oleh pembentukan lapisan penebat zink oksida, yang umumnya dianggap sebagai hasil tindakbalas akhir bagi sel zink-udara, dan bukannya disebabkan oleh sebarang tindakbalas sampingan di antara gel dengan elektrod mahupun dengan elektrolit. Kapasiti sel yang rendah diandaikan berpunca daripada luas permukaan kepingan plat zink yang rendah, rintangan antaramuka disebabkan oleh elektrolit KOH berkeadaan jeli dan struktur gel yang memerangkap air dengan lebih kuat. Lapisan nipis agar berlakur KOH diapitkan di antaramuka-antaramuka elektrod-gel elektrolit bagi memperelokkan sentuhan antaramuka dan pada masa yang sama juga bertindak sebagai penakung elektrolit. Agar merupakan polimer semulajadi yang mesra alam yang diekstrak daripada alga laut dan bersifat membentuk gel. Hasilnya nyata sekali kapasiti sel zink-udara telah digandakan kepada 711, 240 dan 163 mAh, yang dicirikan pada arus discas 5, 50 dan 100 mA masing-masing. Sebagai menambahkan lagi prestasi sel, anod zink berstruktur poros telah diperbuat daripada campuran serbuk zink dan grafit, dan menggunakan larutan agar

bergelatin sebagai agen pengikat (*binder*). Kandungan grafit dan kelikatan larutan agar divariasi untuk mendapatkan komposisi optimum bagi elektrod. Penambahan serbuk grafit ke dalam komposisi elektrod didapati tidak menyumbang terhadap prestasi elektrod disebabkan pembentukan lapisan limpah grafit (*graphite-rich layer*) yang membatasi keporosan elektrod. Penggunaan larutan agar berkelikatan melebihi 5 mg cm^{-3} menyebabkan pembentukan selaput agar yang cukup tebal bagi menebat bahan aktif zink dan akhirnya membataskan kapasiti sel. Dengan menggunakan elektrod zink berstruktur poros, kapasiti sel yang berjaya diperolehi adalah 1910 dan 2066 mAh, yang dicirikan pada arus 0.1 A dan 50 mA masing-masing. Nilai muatan tenaga tentu sel yang sebanding adalah 420 dan 433 Wh kg^{-1}. Prestasi sel pada arus yang dicirikan ini boleh dikategorikan sebanding dengan bateri zink-udara yang terkini. Kajian Kitar Voltammetri (*Cyclic voltammetry*) dilakukan ke atas elektrod zink dan elektrod udara di dalam elektrolit gel untuk menentusah kesan pelikatan elektrolit yang menggunapakai gel hidroponik ke atas kinetik elektrod. Sebagaimana yang dijangkakan elektrolit gel tersebut mengakibatkan rintangan yang ketara ke atas kinetik elektrod hasil daripada keterbatasan elektrolit bebas dan juga struktur gel. Sebaliknya sifat-sifat elektrolit gel ini menghasilkan beberapa ciri yang menarik terutamanya dalam penyelidikan bateri alkali sekunder berasaskan zink. Kedua-dua keterlarutan dan kelincahan (*mobility*) hasil oksidasi zink direndahkan dan dengan ini memperbaiki penyaduran semula (*redeposition*) spesis zinkat (*zincate*) dengan ketara. Penggunaan gel elektrolit juga merencat pembebasan kedua-dua gas oksigen dan hidrogen. Struktur serabut karbon elektrod udara komersil itu didapati tidak begitu sesuai untuk penggunaan elektrolit gel. Ia menghalang elektrolit gel itu daripada menembusi struktur tersebut dan kesannya luas permukaan yang besar elektrod udara itu tidak dapat dimanfaatkan sepenuhnya. Bagi elektrod zink, penggunaan lapisan agar sebagai penakung elektrolit mengurangkan halangan akibat penggunaan elektrolit gel. Untuk elektrod udara pula aplikasi lapisan agar tersebut adalah amat berguna dalam mengekalkan kelembapan elektrod udara sepanjang operasi sel.

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Andai dinobat mewarisi takhta
empunya kerajaan dan jajahan takluk,
namun tanpa ayah bonda di sisi
pastikan suram, sayu hati ini

Walau mahligai tersergam megah
saban ketika diapit pembesar, hulubalang dan dayang
namun diri ini tetap sepi
menanti hadir saudara sepermainan

Manakan dipisah
aur dan tebing
Laila dan Majnun
raja dan permaisurinya

Semerdu kicau burung di taman
selunak gurindam dan syair indah
manakan sama
tawa tangis si kecil

Karya ini diabadikan buat,

Ayah bonda
Hj. Othman bin Mustafa
Hjh. Nya Pon binti Abdul Wahab

Saudara sepermainan
Zarina binti Othman
Rashidi bin Othman
Fazidah binti Othman
Suhana binti Othman

Permaisuriku
Norraba'a binti Mat Noor

Si kecil
Muhammad Aminuddin bin Raihan
Muhammad Anas bin Raihan
Adinda Amin & Anas

Raihan bin Othman
Jumaat
26 Rabiul Akhir 1424
27 Jun 2003

CHAPTER I

Introduction

The *portable paradox* has forced electronics equipment manufacturers, especially those producing electronics telecommunication and computing devices to squeeze more functionality into ever-decreasing volumes. A wide array of consumer portable electronics devices including the computer notebook, cellular telephone, personal digital assistance (PDA), digital image recorder, game devices and music systems are at present merging into a single device. Whilst from the technological point of view the electronic components are becoming more efficient and demand less power, the ever-increasing functionality and density as a whole requires a higher energy and power density storage. A measure of the usefulness of a portable electronics device is the extent to which it can sustain its operation without being plugged into an electrical outlet. Thus the ultimate challenge is now on the battery researchers and manufacturers to seek the suitable candidate. Metal-air batteries are the prospective candidates.

Metal-air batteries are popularly dubbed as *breathing batteries*. They are unique in that they utilize oxygen from the ambient air as one of the electroactive materials. Hence this provides them with a practically unlimited and free oxygen supply. Further the use of atmospheric oxygen does not require storage, which in principle reduces the weight and simplifies the battery design. Consequently, the metal active