**Zinc Oxide Nanostructures in the Zinc Electrode of a Zinc-Carbon Dry Cell**

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**INTRODUCTION**
Zinc oxide (ZnO), a representative of II–VI semiconductor compounds, is a technologically important material. ZnO has a unique position among the semiconducting oxides due to its piezoelectric and transparent conducting properties, high electrical conductivity and optical transmittance in the visible region. These properties make ZnO ideal for applications such as transparent conducting electrodes in flat panel displays and window layers in thin film heterojunction solar cells.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) analysis were performed on a JEOL JSM-6480LV scanning electron microscope.

**MATERIALS AND METHODS**
Zn electrodes from used Zn-C dry cell
Samples of Zn electrodes from Zn-C dry cells that had been used for a complete life period were collected. The surface of the Zn electrode was not treated with any etchant. The inner surface of the Zn electrode that was in contact with the electrolyte was examined using an SEM. Figure 1a shows the Zn casing of the Zn-C dry cell. Figures 1b and 1c show the electrolyte and the C-electrode in an opened Zn-C dry cell.

**EDX analysis was performed on a JEOL JSM-6480LV scanning electron microscope.**

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that was liquid-nitrogen cooled. An accelerating voltage of 25 kV was used with a 1 nm probe with ~1 nA of current on the specimen.

RESULTS AND DISCUSSION

The Zn-C dry cell consists of a zinc casing which acts as the negative terminal and a carbon or graphite rod which acts as the positive terminal. The electrolyte is made up of manganese (IV) dioxide (MnO₂), ammonium chloride (NH₄Cl) and zinc chloride (ZnCl₂). When the external switch is closed, an atom of Zn on the Zn electrode is oxidized to Zn²⁺ ion, liberating two electrons. The reaction which takes place in the dry Zn-C dry cell is as follows:

\[
\begin{align*}
Zn(s) & \rightarrow Zn^{2+} + 2e^- \\
2NH_4^+(aq) + 2e^- & \rightarrow H_2(g) + 2NH_3(aq) \\
2MnO_2(s) + H_2(g) & \rightarrow Mn_2O_3(s) + H_2O(l) \\
Zn^{2+} + 2NH_3(aq) & \rightarrow Zn(NH_3)_2^{2+}(aq)
\end{align*}
\]

Although there could be several other reactions taking place, the overall reaction in a Zn-C dry cell can be represented as:

\[
Zn(s) + 2MnO_2(s) + 2NH_4^+(aq) \rightarrow Mn_2O_3(s) + Zn(NH_3)_2^{2+}(aq) + H_2O(l)
\]

One of the reactions that could lead to the formation of ZnO in the Zn electrode is:

\[
H_2O(l) \rightarrow H^+(aq) + OH^- (aq) \\
Zn(s) + 2OH^- (aq) \rightarrow ZnO + H_2O + 2e^- 
\]

A reaction of this type is likely to result in the formation of ZnO. It has also been reported earlier by Wu et al. [7] that Zn(OH)₂ decomposes and forms a nucleus for the growth of ZnO crystals when the solution was placed into the 50°C water bath.

Figures 2a and 3 show the SEM image of the Zn electrode of a completely used 1.5 volt Zn-C dry cell. Each hierarchical structure of ZnO consists of many nanorod arrays as its secondary structure. From the magnified SEM image we can see symmetrical rod-arrays. These arrays of rods comprising the hierarchical structure can be divided into two categories, namely primary rod arrays (PRAS) and secondary rod arrays (SRAS).
Figure 5: Schematic showing the details of how the PRAS and the SRAS grow and the formation process of the hierarchical structure.

Arrays (SRAS) [7]. The PRAS are formed into a line while the SRAS look like branches coming out of the PRAS. SRAS which are located at both ends of the PRAS form an angle of $60^\circ$ with each other, while the SRAS located at the inner area of PRAS are parallel to each other. The tips of the ZnO rods in both PRAS and SRAS are pointed. According to previous work, the first formed stem can provide its six prismatic planes as the platforms for the later growth of the branches. The legs of the star-like structures have a thickness of just less than 100 nm. The legs of the star-like structures preferentially grew along the [0001] direction [8-10]. The lengths of the legs are around 0.5 µm (refer to Figures 2a and 3).

The EDX analysis of the ZnO structures is shown in Figure 4. Apart from Zn (at. % = 48.07 %) and O (at. % = 44.79 %) there is also the presence of a small amount of Cl (at. % = 7.14 %). As discussed earlier the electrolyte in the Zn-C dry cell is composed of manganese (IV) dioxide (MnO$_2$), ammonium chloride (NH$_4$Cl) and zinc chloride (ZnCl$_2$). Cl in the ZnO structures has possibly come from the electrolyte. The Cl in the ZnO structures must have come from the Cl in the ammonium chloride (NH$_4$Cl) and zinc chloride (ZnCl$_2$) in the electrolyte. This suggests that the ZnO structures are not very pure and have trace amounts of elements such as Cl.

The ZnO prefers to grow along the c-axis and the (0001) plane. The first formed ZnO stem provides its six prismatic planes as the platforms for the later growth of the branches. The process of formation of the hierarchical structure starts with the generation of the nanorods. The nanorods after their formation are aligned together and fused into a wall to form the PRAS. For the rods located on each end of a PRA, two of their six planes cannot act as a platform due to the spatial barrier (marked as green lines with arrow heads at both ends in the schematic diagram in Figure 2b). In contrast, for the rods located inside a PRA, only two of the six planes can act as the platform for the later growth of the SRAS (refer to Figure 2b) [7-10].

Initially the formation of ZnO is very slow and gradually the small ZnO particles fuse to form the ZnO nanorods. First the nanorods were formed along the [0001] direction. Then, the formed rods aggregated side by side to reduce their surface energy and finally fused to form a wall. However, when the rate of the growth of ZnO structures became very rapid, the prismatic planes of the ZnO rods that have already formed act as the substrates to compensate the rapid growth rate. This is the stage when the secondary rod arrays are formed [7]. The schematic in Figure 5 shows the details of how the PRAS and SRAS are formed.

Apart from the hierarchical structure, rod-like structures of ZnO could also be seen. The rod-like structures of ZnO are mostly nanostructured. Figures 6 a-e clearly show the formation of ZnO nanorods in the Zn electrode of a fully used Zn-C dry cell. It can be seen from the EDX analysis of the ZnO nanostructures that they are not very pure and stoichiometric. The
EDX analysis shows presence of other elements such as Cl, K and Pb. The at. % of oxygen in the nanostructures is very high. EDX analysis of the nanorods was also done and is reported in Figure 7. In one of the samples the at.% of oxygen was 43.45 whereas the at.% of zinc was 23.38. This clearly proves that the nanostructures are not of high purity ZnO and also not stoichiometric. Apart from this, elements like Cl (11.59 at.%) were also seen in the ZnO structure.

CONCLUSIONS
There is clear indication of the fact that the Zn casing of the Zn-C dry cell gets oxidized due to the electrochemical reaction with the electrolyte of the cell forming ZnO nanostructures. The nanostructures of ZnO are of various shapes. Rod-like, wire-like and star-like nanostructures of ZnO have been found in the surface of the Zn electrode of the Zn-C dry cell that is in contact with the electrolyte. The ZnO nanostructures do not have very high purity and are also not highly stoichiometric.

REFERENCES

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