

**EFFECT OF NON-STOICHIOMETRY ON THE ELECTRODE PROPERTIES OF ZIRCONIUM DISELENIDE IN LITHIUM/POLYMER ELECTROLYTE BATTERIES (EXTENDED ABSTRACT)****R. YAZAMI\***

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In order to study the effect of non-stoichiometry on both the transport and chemical or electrochemical intercalation properties of the dichalcogenides of the IVb group of transition metals, we turned our attention to zirconium diselenide, having the general formula  $ZrSe_y$ .

In its existing domain of stoichiometry  $1.85 < y < 1.95$ , we have shown that  $ZrSe_y$  undergoes a composition induced semiconductor-to-metal transition when the selenium content decreases below 1.90 [1]. According to Gleizes and Jeannin [2], the departure from stoichiometry is mainly due to selenium vacancies in the semiconducting-like compounds ( $y > 1.90$ ), and to interstitial zirconium associated with selenium vacancies in the metallic ones ( $y < 1.90$ ). A lithium intercalation induced semiconductor/metal transition has also been observed in  $Li_xZrSe_{1.94}$  when the amount of lithium exceeds a threshold value of about 0.4 [3].

The properties of  $ZrSe_y$  as cathode material in a solid state lithium battery using poly(ethylene oxide) as electrolyte support are strongly dependent on the stoichiometry of the host compound [4]. We have used both intermittent galvanostatic titration and very slow scan voltamperometry techniques to determine the electrode behaviour during the lithium intercalation. We observed two types of discharge curves which are characteristic of the two electronic states of the material:

(i) In the semiconductor material ( $y = 1.915$ ), a first step of lithium intercalation ( $x < 0.15$ ) is evidenced by the appearance of a small 2.25 V plateau in the titration curve (Fig. 1(a)) associated with a current peak at that voltage in the voltamperogram (Fig. 1(b)). This was attributed to a

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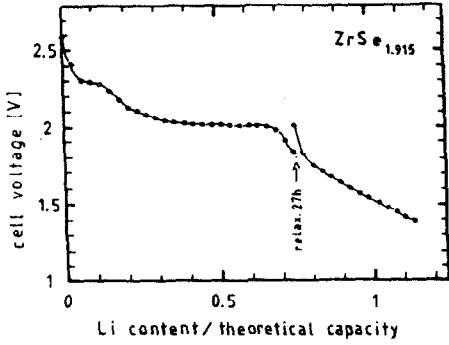


Fig. 1(a).

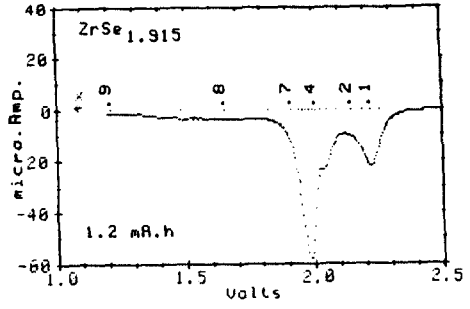


Fig. 1(b).

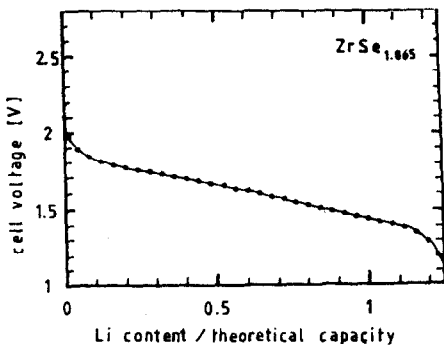


Fig. 2(a).

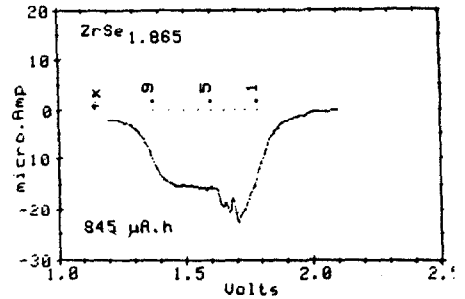


Fig. 2(b).

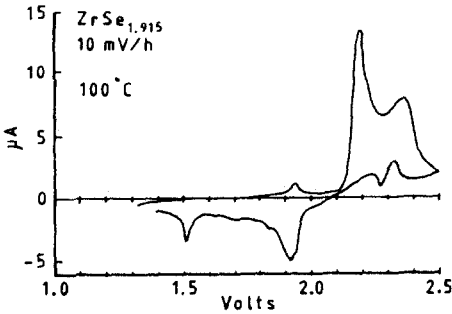


Fig. 3(a).

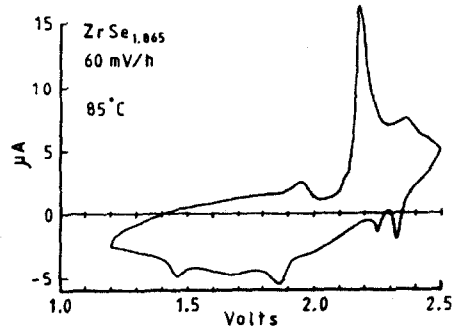


Fig. 3(b).

Figures 1(a) and 2(a) show the open circuit voltage from galvanostatic intermittent measurements at the  $C/30$  rate with 3 h relaxation, for a semiconducting and a metallic host. Figures 1(b) and 2(b) show the first discharge with very slow scan voltamperograms recorded at  $-10 \text{ mV h}^{-1}$  for the same host compositions. Figure 3 (a), (b) shows the second charge and the third discharge for the  $\text{ZrSe}_{1.915}$ , and the 14th charge and 15th discharge for the  $\text{ZrSe}_{1.865}$  compound at  $\pm 10 \text{ mV h}^{-1}$  and  $\pm 60 \text{ mV h}^{-1}$  respectively.

preferential localization of lithium ion in the vicinity of the selenium vacancies found in  $\text{ZrSe}_{1.915}$  in the early step of intercalation. Then lithium occupies the octahedral sites in the Van der Waals gap leading to a second 2.05 V plateau and a current peak at 1.95 V in the titration curve and voltamogram, respectively. We have observed an enhancement of the lithium diffusivity for  $x \approx 0.6$ , correlated to the semiconductor-to-metal transition induced by lithium intercalation.

(ii) Concerning the metallic-like cathode material ( $y = 1.865$ ), the titration curve (Fig. 2(a)) shows a uniform potential decrease characteristic of an intercalation electrode reaction with a random lithium distribution within the Van der Waals gap. This is also observed in the corresponding voltamogram (Fig. 2(b)), in which only one very broad current peak, from 1.5 to 1.8 V, is found.

Another striking difference between the two electrode materials is encountered during the battery cycling tests using the voltamperometry technique. An evolution of both anodic and cathodic behaviours is found, depending on the number of cycles and the upper battery voltage reached during recharge.

In the semiconductor electrode, we have found good reversibility of the current peak associated with the lithium occupancy of the Van der Waals gap in the voltage range 1.7 - 2.25 V. For higher potentials, an irreversible electrode decomposition occurs as a selenium transfer into the polymer electrolyte takes place. Then the 2.25 V reduction peak is strongly modified as the 1.95 V peak tends to disappear (Fig. 3(a)).

During battery charge up to 2.5 V with the metallic electrode, we observed two oxidation peaks, a broad one at 2.37 V and a small one at 2.47 V (Fig. 3(b)). These peaks are responsible for the appearance of new reduction peaks at 2.34 V and 2.26 V which were not present in the first discharge voltamperogram (Fig. 2(b)). So, the high voltage oxidation induces a dramatic change in the electrode behaviour, which is now closer to that of the semiconducting material, with a characteristic reduction peak at 1.9 V associated with the narrow oxidation peak at 2.18 V. We suggest that the reduction peak at 2.26 V could be associated with lithium intercalation, with preferential localization close to the selenium vacancies created during the oxidation peak at 2.34 V. For the new reduction peak at 2.36 V associated with the 2.48 V oxidation peak, we do not exclude the possibility of reduction/oxidation of the interstitial zirconium from  $\text{Zr}^{3+}$  to  $\text{Zr}^{4+}$  with perchlorate ion transfer from the electrolyte ( $\text{P}(\text{OE})_8\text{LiClO}_4$ ) to the electrode.

In conclusion, the non-stoichiometry found in zirconium diselenide strongly influences its electrode properties in solid state lithium batteries. Our cyclability study emphasizes the role of both the electronic characteristics and the battery voltage on the electrode evolution with increasing cycle number. It seems that reciprocal semiconductor/metal transitions can be induced by either lithium or perchlorate ion intercalation in the corresponding electrodes. Further investigations are in progress to confirm our hypothesis.

**References**

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