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Negative Electrode for Lithium Battery in Room Temperature Molten Salt

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Room temperature molten salts (RTMS) based on 1-methyl-3-ethylimidazolium chloride (MEICl) provides an interesting ionic medium for lithium battery application due to its wide electrochemical window, high ionic conductivity and good safety feature during short circuiting¹⁻².

Materials intercalated with lithium ions such as LiCoO_2 , LiMn_2O_4 and LiNiO_2 ^{3,4} had been used successfully as positive electrode materials in RTMS in previous studies. However, a suitable negative electrode material for the lithium battery is more difficult to find in RTMS. Although carbonaceous materials had been widely investigated as intercalation anodes for lithium-ion secondary battery in the organic electrolyte system, its application as anode material in RTMS led to a very serious exfoliation problem due to the irreversible co-intercalation of other ions present in the melt that reduced the subsequent performance of the anode during cycling.

There are two approaches to solve the above problem. The first approach is by coating the surface of graphite with a metallic alloy that prevents the intercalation of other organic ions that causes the exfoliation problem.

The second approach is the use of metallic alloys instead of graphite as the material for negative electrode material.

From the CV studies of the graphite electrodes in acidic RTMS (a mole composition of 66.7% AlCl_3 and 33.3% MEICl), aluminum was found to deposit at a potential of 0 V coupled with a stripping peak at 0.13 V. Thus, the bulk deposition of Al was conducted at a constant current density of 4mA/cm^2 while the potential was kept near -0.05V . The resulted Al films as observed by SEM shows the formation of a uniformly distributed and compacted aluminum film on graphite from the deposition in the acidic RTMS.

To investigate the effects of the Al coating on the intercalation-deintercalation performance of the graphite electrode, especially the initial irreversible capacity related to the side-reaction and co-intercalation of EMI^+ , galvanostatic cyclings were carried out using bare graphite and Al-coated graphite electrodes in a cell of C/LiCl buffered RTMS/Li. The voltage profiles at a constant charge-discharge current of 4mA/cm^2 were shown in Fig.1. The resulted Al-coating graphite electrodes have been used as negative electrode in a lithium battery with LiCl buffered AlCl_3 -MEICl RTMS. The Al film distributed on the surface of the graphite depressed the side reaction occurred at potential more positive than -1.6V and blocked the co-intercalation of MEI^+ . Therefore the reversibly capacity of the graphite have been increased from 26% to 57% in the first cycle and the cycling performance of the graphite negative been improved.

A new room temperature molten salt (RTMS) (1-methyl-3-ethylimidazolium / AlCl_3 / SnCl_2 (3:2:0.5)) was developed to deposit tin on copper electrode. Different tin crystallites were deposited at different temperatures, giving widely different performance of the lithium cell assembled (Sn (Cu)/LiCl buffered MEICl- AlCl_3 RTMS/lithium). Tin film deposited at 50°C or higher gave desirable a crystal structure (Fig. 2) and an improved performance than those obtained at lower temperatures.

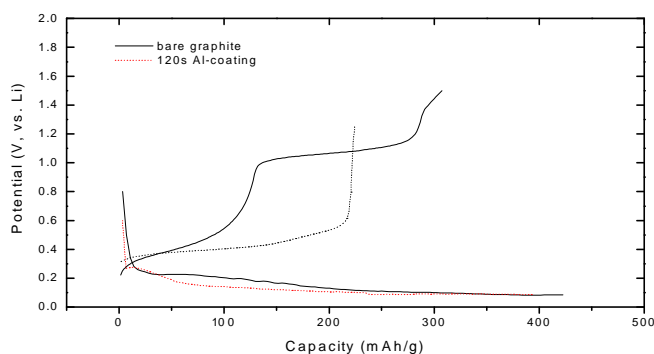


Figure 1. Galvanostatic first cycle charge-discharge curves for bare graphite electrode and 120s Al-coated graphite electrode in buffered RTMS (AlCl_3 :MEICl:LiCl = 1.2:1:0.2) at a constant current of 4mA/cm^2 .

An average capacity of 140mAh/g , coulombic efficiency around 85% and more than 200 cycles were obtained at a low c.d. (0.4mA/cm^2). The improvement is attributed to the deposition of small and regular tin crystallites that allows reversible insertion and removal of lithium from a more stable crystal structure without a significant volume change during cycling.

As a summary, the approach using Al as coating for the graphite electrode produces a negative electrode with a higher current and the use of tin provides a longer lifetime for cycling at a lower average capacity.

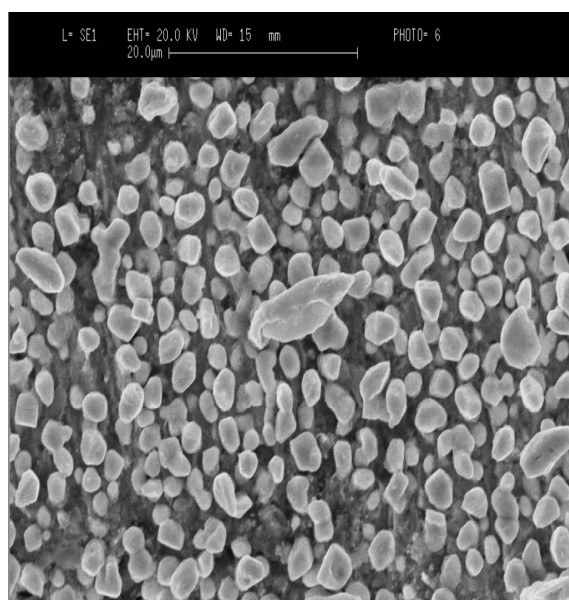


Figure 2. SEM micrograph of tin films deposited at 50°C at a constant current of 3.3mA/cm^2 .

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