

COMPARATIVE STUDY OF ANODES BASED ON CARBON NANOMATERIALS AND LI METAL IN CHEMICAL POWER SOURCES WITH GEL- ELECTROLYTE

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Introduction

The given work is devoted to development Li and Li-ion batteries with gel polymer electrolyte which can be used for mobile radio communication, notebooks, non-polluting electromobiles and military technical equipment.

The best material for anode production in chemical power sources (CPS) is still considered Li having the most negative electrode potential (-3.045 V in water solution), the highest specific energy (11.8 W*h/g) and high specific capacity (3.86 A*h/g). For the first time interest to development of power sources with use of Li metal has appeared in 1960th years, and occurrence of the primary CPS with aprotic nonaqueous electrolyte solutions date to the beginning of 1970th years.

If development of primary elements with Li- anode has crowned rather fast success, and such elements have strongly taken place as power sources of the portable equipment civil and special purpose, then the creation Li- batteries was accompanied by the tragically events caused by combustions and explosions such CPS. The way out has been found at replacement of Li metal by carbon which appeared very convenient matrix for Li intercalation.

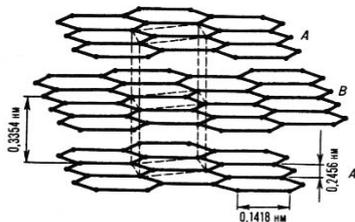
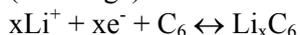


Fig. 1. The carbon anode of Li- ion batteries capable intercalated (charge) and deintercalated (discharge) Li ions on reaction



The specific volume of many graphitized carbon materials at introduction of sufficiently large amount of Li is changes no more than on 10%.

The potential of carbon electrodes containing not sufficiently large amount intercalated Li ($x \sim 0.1$), can be more positively of Li electrode

potential on 0.5-0.8 V. In order to voltage of battery was sufficiently high, cobalt oxide is using as cathode active material. LiCoO_2 has potential near 4 V opposite Li electrode so that batteries working voltage has characteristic value of 3 V.

At discharge of battery Li deintercalation from carbon material (on negative electrode) and Li intercalation in oxide (on positive electrode) are occurs. Processes go to reverse direction at charge. Thus, in all system there is no Li metal (zero - valent), and processes of discharge and charge are come to carry of Li ions from one electrode to another. For this reason such batteries have received the name "lithium - ion".

In spite of the fact that Li - ion batteries are more fireproof, than lithiums, they too have lacks, namely during process Li intercalation - deintercalation they reduce the capacity. Development of electrolytes systems with carbon nanomaterials which would differ by increased stability of work therefore is of interest. One of such directions is replacement of liquid organic electrolyte on polymeric that allows improving characteristics and decreasing electrolyte outflow on depressurization.

Results and discussion

In present work gel polymer electrolyte (GPE) based on polyethylene oxide (PEO, $M_w = 500\ 000$) for Li-ion batteries is developed. The electrochemical system contains: the cathode - LiCoO_2 ; the anode - carbon of the layered structure such as "hard carbon" (Fig. 1); liquid organic electrolyte - 1 M LiPF_6 in a mix ethylene carbonate/ dimethyle carbonate/ ethylemethyl carbonate (EC/DMC/EMC) (40:30:30); GPE - the same composition with introduction 1 w/w % PEO.

The electrolyte viscosity increases for the order at introduction 1 w/w % PEO. At analyzing of viscosity change from temperature, viscosity of liquid electrolyte increases almost in 5 times at -20°C and one of GPE only in 1.5 times at 20°C .

The volume conductivity of electrolytes in temperature range from -20 up to 30°C has been measured. It is found, that volume conductivity of electrolyte is reduced insignificantly (in 1.3 times)

at introduction 1 w/w% PEO in all interval of temperatures.

Prototypes of batteries - disk elements Li/electrolyte/LiCoO₂ and C/electrolyte/LiCoO₂ (in comparison with liquid) with developed GPE have been assembled and their charge - discharge tests in voltage interval 2.8 ÷ 4.2 V are carried out (Fig. 2).

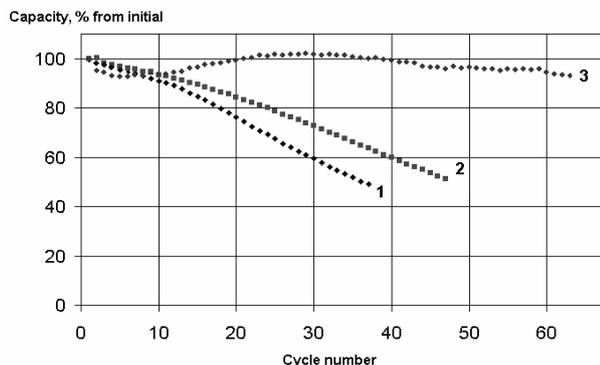


Fig. 2. Resource of disk batteries C/electrolyte/LiCoO₂ with liquid electrolyte (1) and GPE (2); Li/GPE /LiCoO₂ (3).

Fig. 2 show that the battery with Li- electrode has carried out 63 charge - discharge cycles. The loss capacity was at the initial stage of tests, and then capacity of the battery was restored and after 20 cycles even began to exceed initial one, that Fig. 2 show. Tests of Li-ion batteries have shown the worse results comparison with lithium. So the battery with liquid electrolyte loses the capacity fastest. As to batteries with GPE (№ 2), gel - electrolyte improves Li-ion battery cycling. The given effect is possible to explain to the following. The liquid electrolyte based on EC, DMC and EMC decays on carbon anode surface during electrochemical reaction. The entrance in space between graphen planes in width of 0.335 nanometers is hammered by products of decomposition of molecules of solvent (Fig. 3).

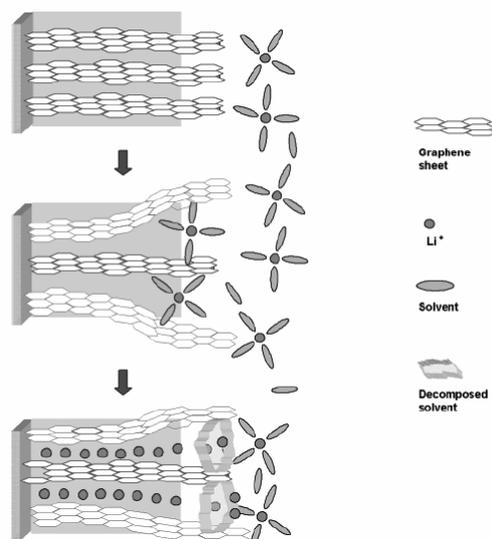


Fig. 3. The scheme of mechanism of formation passivated layer at decomposition $Li(solv)_x C_y$ [1].

Intercalation and deintercalation of Li in this area of carbon anode is complicated. In case PEO process of solvent decomposition is reduced. Except for good solvating abilities to Li ions are caused by atoms of oxygen, units of PEO also have not polar fragments which will well cooperate with edges of graphen planes. Thus, the blanket will be created on carbon anode surface and will be prevented direct contact of solvent molecules and graphen planes and to pass Li ions.

Conclusions

Thus, in present work it is shown, that presence molecules PEO (1 w/w%) at liquid electrolyte improves electrochemical characteristics of Li - ion battery; raises viscosity of electrolytes systems on the order, thus, reducing speed of electrolyte outflow in case of depressurization of power source that increases safety the CPS.

References

1. Besenhard J.O., Winter M.; Yang J.; Biberacher W. J. Power Sources, 1993, 54, p.228.