

Anodic dissolution of aluminium in nonaqueous electrolytes

K. V. Rybalka and L. A. Beketaeva

A.N. Frumkin Institute of Electrochemistry, Academy of Sciences of Russia, Moscow (Russian Federation)

(Received July 1, 1992; in revised form November 5, 1992; accepted November 13, 1992)

Abstract

The anodic dissolution of Al electrode in nonaqueous electrolytes has been studied. At the discharge rate of 1 mA/cm² the available capacity of 30 mAh/cm² was obtained in 1 M LiAlCl₄ solution in propylene carbonate. For the 1 M LiClO₄ solution in a mixture of propylene carbonate and dimethoxyethane at the same rate the available capacity exceeds 100 mAh/cm². Al can be considered as a promising anode material for developing nonaqueous Al batteries.

Introduction

Aluminium is obviously the most interesting metal to be used in power sources. The attractive feature of Al is the high negative value of its standard potential which is about one volt more negative than the standard potential of zinc, largely used as an anode material in power sources. Among all the metals Al takes the first place by the quantity of electricity provided by unity of volume (8.03 Ah/cm³). This value is almost as a factor 4 higher than that for lithium. By its gravimetric quantity of electricity Al yields only slightly to lithium.

The huge deposit of Al must be also mentioned. By its widespreadness in the earth crust Al takes the first place among the metals and the third one among all the chemical elements [1].

The totality of physical and chemical properties of Al in combination with its almost unlimited deposit explains the interest shown for Al as anode for power sources.

The use of aqueous electrolytes for power sources with Al anode is complicated due to the high negative value of the standard potential of Al and hence to an inevitable active hydrogen evolution. The rate of corrosion of Al for instance in 30% NaOH solution is 17 mg/(cm² h), corresponding to corrosion current density 50 mA/cm² [2].

In nonaqueous electrolytes the self-dissolution of Al will be certainly eliminated and one can suggest that in this case all the advantages of Al anode can be realized. The practical utilization of Al anode in power sources is impeded by the presence of an oxide film on its surface [3]. It was shown [4] that even in very dry electrolytes (<1 ppm of free water) the passive film on the Al surface initially free of oxides is restored in a few seconds.

In the present study the possibility to decrease the harmful influence of the oxide film on the anodic dissolution of Al is examined with the purpose to develop an efficient Al anode for battery systems.

Experimental

The working electrode was a pure Al (99.999) 28 mm in diameter and 0.4 mm thick. The maximum diameter of the working surface of Al was 20 mm. The Al electrode before the measurements was degreased with acetone.

As a cathode MnO_2 electrode was used. The cathode-active mass consisted of 85% of MnO_2 , 10% of acetylene black and 5% of polytetrafluoroethylene. Acetone was used as a solvent for making the cathode paste. The cathode paste was pressed onto titanium grid welded to the titanium current collector. The cathode was dried during 3 days in vacuum at 100 °C. All the investigations were conducted in a polyethylene cell presented in Fig. 1. As it follows from the Fig. the anode and cathode are fixed in parallel to each other. To the back side of the anode a stainless-steel washer is pressed, providing its protection against mechanical damage. This washer ensures also an electrical contact with the working electrode. The anode and cathode are tightly pressed to the body of the cell using polyethylene nuts. The cell design allows to change the value of the working surface using special gasket between the anode and the body of the cell.

The Ag wire covered with AgCl layer was used as a reference electrode and mounted in a polyethylene holder introduced in the upper part of the cell.

The Al electrode was chemically treated before the measurements on purpose to decrease the influence of the passivating oxide film on its anodic dissolution. All measurements were carried out at ambient temperature (22 °C) in nonaqueous electrolytes containing additives. The content of free water was less than 6 ppm.

Results and discussion

The initial surface state of Al electrode determines completely its electrochemical behaviour, in particular its anodic dissolution. The potential of the Al electrode in 1 M LiAlCl_4 in propylene carbonate (PC) as a function of time is shown in Fig. 2. Curve (1) corresponds to an untreated electrode, curve (2) to a pretreated one. As it follows from this Fig. the pretreatment of the Al electrode allows to shift considerably the value of its stationary potential to the negative side. These results show that the

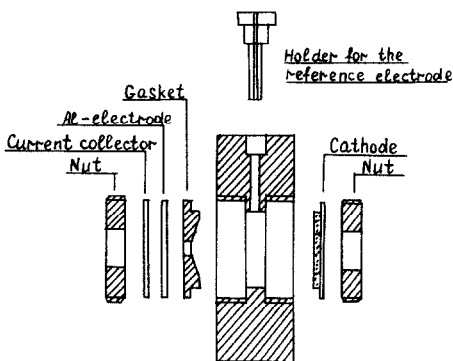


Fig. 1. Cell construction.

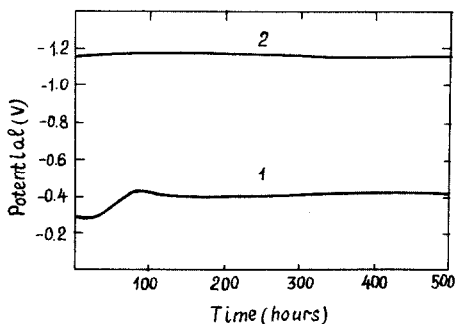


Fig. 2. Potential of the Al electrode in 1 M LiAlCl_4 in propylene carbonate as a function of time: (1) untreated electrode and (2) pretreated electrode.

pretreatment leads to the destruction (at least partial) of the oxide film on the Al. The value of the stationary potential of the Al electrode reached after it pretreatment remains constant during a long time. Similar results were obtained for the Al electrode in 1 M LiClO₄ in the mixture of PC and dimethoxyethane (DME).

The anodic behaviour of Al was studied using galvanostatic technique. The results only for pretreated electrodes are presented. In the absence of pretreatment no available capacity can be obtained due to instantaneous passivation of the Al electrode at its polarization. The discharge curve for the Al electrode in 1 M solution of LiAlCl₄ in PC is presented in Fig. 3. The initial drop of potential, when the discharge current of 1 mA/cm² is applied, is about 100 mV. During the anodic polarization of the Al electrode a light shift of its potential in the negative side is observed. It is obviously due to the additional destruction of the oxide film on the Al during its discharge. The shape of the discharge curve in Fig. 3 can be explained by the competition of two processes occurring on the Al electrode: (i) destruction of the oxide film and (ii) the passivation of the electrode by products of its anodic dissolution. The available capacity of the Al electrode in LiAlCl₄ solution in PC makes up about 30 mAh/cm². Close values of available capacity were obtained at the discharge rate of 0.1 and 0.3 mA/cm².

The overvoltage of the process of the anodic dissolution of Al in LiAlCl₄ solution in PC as a function of the discharge current is shown in Fig. 4. The curves in this Fig. correspond to two different state of discharge of the electrode. Curve (1) to the state of discharge of 8 mAh/cm², and curve (2) to 24 mAh/cm², i.e. to the initial and final part of the discharge curve presented in Fig. 3. Only a slight increase of the overvoltage with the discharge of the electrode can be mentioned.

The available capacity as it was mentioned above was measured at a discharge rate of 1 mA/cm². It should be emphasized that the short-term polarization of the Al electrode by currents up to 5 mA/cm² does not change the value of its capacity.

The substitution of the LiAlCl₄ electrolyte by LiClO₄ allows to increase considerably the available capacity of the Al electrode. Figure 5 shows the voltage-time plot for the discharge of the Al electrode in 1 M LiClO₄ solution in the mixture of PC and DME. This Fig. indicates that the available capacity of the Al electrode in this case is much higher than in the LiAlCl₄ exceeding 100 mAh/cm². High stability of the discharge potential of the Al electrode is observed in LiClO₄ electrolyte. The discharge

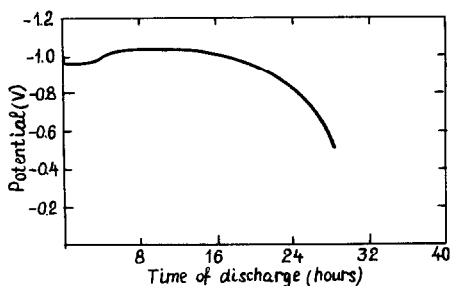


Fig. 3. Discharge curve of the Al electrode in 1 M LiAlCl₄ in propylene carbonate; discharge current 1 mA/cm².

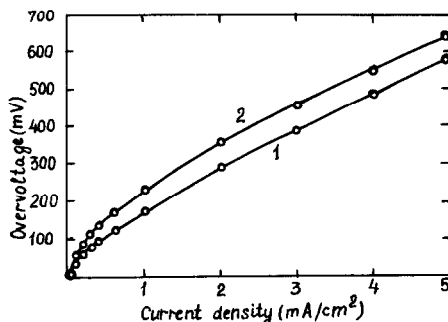


Fig. 4. Plot of overvoltage of the anodic dissolution of Al in 1 M LiAlCl₄ in propylene carbonate vs. current density for two states of discharge: (1) 8 mAh/cm² and (2) 24 mAh/cm².

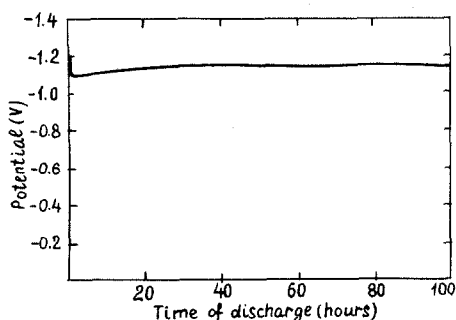


Fig. 5. Discharge curve of the Al electrode in 1 M LiClO_4 in a mixture of propylene carbonate and dimethoxyethane; discharge current 1 mA/cm^2 .

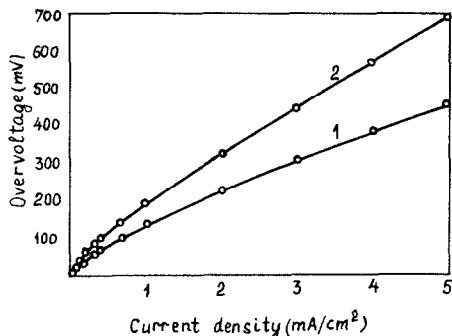


Fig. 6. Plot of overvoltage of the anodic dissolution of Al in 1 M LiClO_4 in a mixture of propylene carbonate and dimethoxyethane vs. current density for two discharge states: (1) 30 mAh/cm^2 and (2) 100 mAh/cm^2 .

of the cell in 1 M LiClO_4 solution was limited by the cathode. Therefore, the total value of the capacity could not be obtained because we avoided to replace the waste cathode by a new one during the discharge.

The dependence of the overvoltage of the process of anodic dissolution of Al on the current density is shown in Fig. 6. Curve (1) in this Fig. is obtained for the initial part of the discharge curve in Fig. 5 and corresponds to the state of discharge of the Al electrode equal to 30 mAh/cm^2 . Curve (2) corresponds to the state of discharge, 100 mAh/cm^2 . Comparison of these data with the overvoltage/current density plot for the dissolution of Al in 1 M LiAlCl_4 in PC (Fig. 4) shows that for close values of state of discharge the overvoltage of Al dissolution in LiClO_4 is lower than in LiAlCl_4 . As in the case of LiAlCl_4 the anodic polarization of Al by current up to 5 mA/cm^2 does not affect the capacity of the electrode obtained at the given rate of discharge.

The open-circuit voltage (OCV) for the Al/ MnO_2 system in 1 M LiAlCl_4 in PC is equal to 2.0 V.

Conclusions

Al electrode ensures acceptable values of the available capacity and discharge current in nonaqueous electrolytes. This performance of the Al electrode together with high values of OCV for Al with traditional cathode systems allows to consider it as a promising anode material for developing nonaqueous Al batteries.

References

- 1 H. Remy, *Lehrbuch der anorganischen Chemie*, Akademische Verlag, Leipzig, 1960.
- 2 A. V. Kuzmina and L. L. Kuzmin, *J. Appl. Chem. USSR*, 36 (1963) 335.
- 3 P. A. Malachuk, in A. J. Bard (ed.), *Encyclopedia of Electrochemistry of the Elements*, Vol. 6, Marcel Dekker, New York, 1976, p. 63.
- 4 L. Bai and B. E. Conway, *J. Electrochem. Soc.*, 137 (1990) 3737.