Technical University of Denmark

DTU

Electroless Growth of Aluminum Dendrites in NaCl-AlCl3 Melts.

Li, Qingfeng; Hjuler, H.A.; Berg, Rolf W.; Bjerrum, Niels J.

[Link back to DTU Orbit](#)

DTU Library
Technical Information Center of Denmark

Electroless Growth of Aluminum Dendrites in NaCl-AlCl₃ Melts

Li Qingfeng, H. A. Hjuler,* R. W. Berg, and N. J. Bjerrum

Molten Salts Group, Chemistry Department A, The Technical University of Denmark, DK-2800 Lyngby, Denmark

ABSTRACT

The spontaneous growth of aluminum dendrites after deposition was observed and examined in sodium chloride-aluminum chloride melts. The concentration gradient of AlCl₃ in the vicinity of the cathode surface resulting from electrolysis constitutes a type of concentration cell with aluminum dendrites as electrodes. The short-circuit discharge of the cell is found to be the driving force for the growth of aluminum dendrites. Such a concentration gradient is proposed to be one of the causes for dendrite formation in the case of metal deposition.

Within the framework of a research program for secondary batteries with NaAlCl₄ saturated with NaCl as electrolyte, aluminum anode and metal sulfide cathode (1), we undertook the electrochemical study of aluminum dendrite formation from the melt. Aluminum dendrite formation during deposition has been the subject of many investigations (2-5), and is to be discussed in a following paper (6). As many authors observed, an aluminum anode was found to dissolve at a higher current efficiency than expected for a three-electron reaction. This was initially attributed to the formation of subvalent aluminum ions (7), but subsequently to the corrosion of aluminum after electrolysis caused by impurities in both NaCl-AlCl₃ (8) and BuPyCl-AlCl₃ (9-11) melts. However, there appears to be another type of problem in connection with the stability of aluminum after electrolysis, i.e., the spontaneous growth of aluminum dendrites on aluminum deposits after electrolysis. The present paper is devoted to an examination of this strange phenomenon.

Experimental

AlCl₃ from Fluka was further distilled as described previously (12). The used NaCl was of analytical grade and dried at 200°C for 40h before use. This method will not remove all traces of moisture in NaCl, but it was found sufficient in the present investigation. Weighings and salt mixing were performed inside a dry-air-filled glove box (dew point < −50°C). The mixtures contained in evacuated, sealed test cells were liquefied by heating in a rocking glass-furnace overnight before deposition experiments started. The molten baths looked colorless but became slightly yellow after being used several times.

Part of the test cell is shown in Fig. 1. The whole cell is the same as described previously (13). A square Pyrex tube was used in order to help the observation of the aluminum deposits. The test electrode with a tungsten lead was made of a glassy carbon rod (Type V10 from Le Carbone Lorraine) of 3 mm diameter sealed under vacuum into Pyrex tubing, then cut and polished to a mirror-like finish. An aluminum rod of 99.999% purity placed on a tungsten wire was used as the counterelectrode.

Before use, all the cells were washed in 33% NaOH solution and then in distilled water, followed by washing with a mixture of concentrated H₂SO₄, 90% H₃PO₄ and 65% HNO₃ (100:121:29 on a volume basis). The cells were finally washed thoroughly in distilled water and dried at 110°-120°C in vacuum overnight. Aluminum deposits were obtained by constant current electrolysis. The current was delivered by a chronoamperostat built in the authors' laboratory. The potential-time curves were recorded by using a X-T recorder.

Experimental Observations

The appearances of the aluminum deposits on the glassy carbon electrode were quite different from each other, depending on the depositing conditions, mainly on current density and melt composition. Generally, dendritic or needlelike deposits were formed at high current densities from the NaAlCl₄ melt saturated with NaCl. However, it was also observed that after electrolysis aluminum den-

drites often appeared and grew more and more on the electrode surface after an induction period. The induction periods varied from several minutes to several hours for different current densities of deposition, and seemed to be in inverse proportion to the current density of deposition. The amount and growth rate of aluminum dendrites formed after electrolysis seemed to increase with increasing current density of deposition.

Figure 2 shows a sequence of typical dendrite growing after deposition electrolysis at 57 mA/cm² for 8 min in NaAlCl₄ saturated with NaCl at 175°C. Figure 2(a) shows the aluminum deposit immediately after electrolysis. It looked porous with a bit of roughness. Figure 2(b) shows the aluminum deposit 18 min after electrolysis was stopped by breaking the circuit. More dendrites appeared and developed on the aluminum deposit. Figure 2(c) shows the deposit after electrolysis had been stopped and the cell left open-circuited for 20 min. The aluminum dendrites grew very fast as soon as the growth had started. Figure 2(d) shows the deposits 21 min after electrolysis stopped. The dendrites thus became bigger and bigger.

In the above mentioned case, the cell voltage during deposition was ca. 400 mV. If the electrolysis was continued, dendrites would certainly appear anyway (at A), and then the cell voltage would go down (at B) when large dendrites were formed, as shown in Fig. 3(a). If the electrolysis was stopped (at C) before dendrites became visible, the voltage remained excessively high for a certain period until large dendrites were formed [at B, Fig. 3(b)]. If
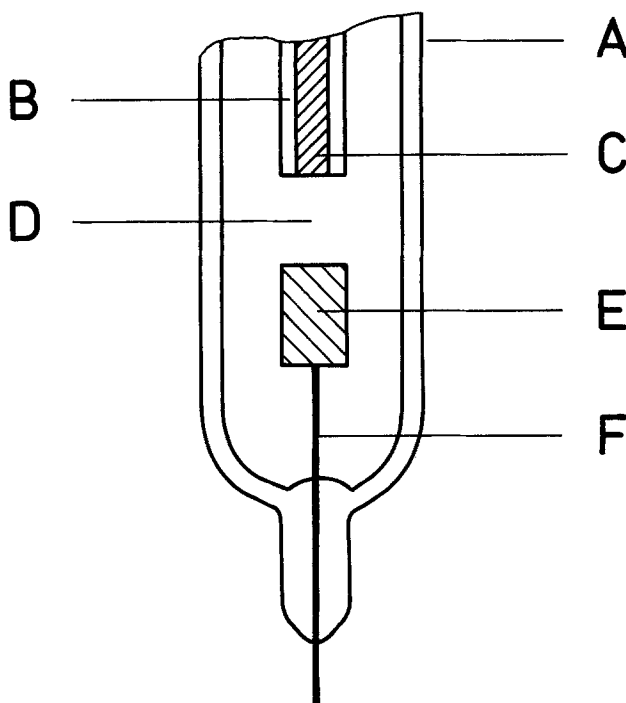
Fig. 1. Part of test cell: A, square Pyrex tube; B, glass covering; C, glassy carbon electrode; D, melt; E, aluminum electrode; and F, tungsten lead.

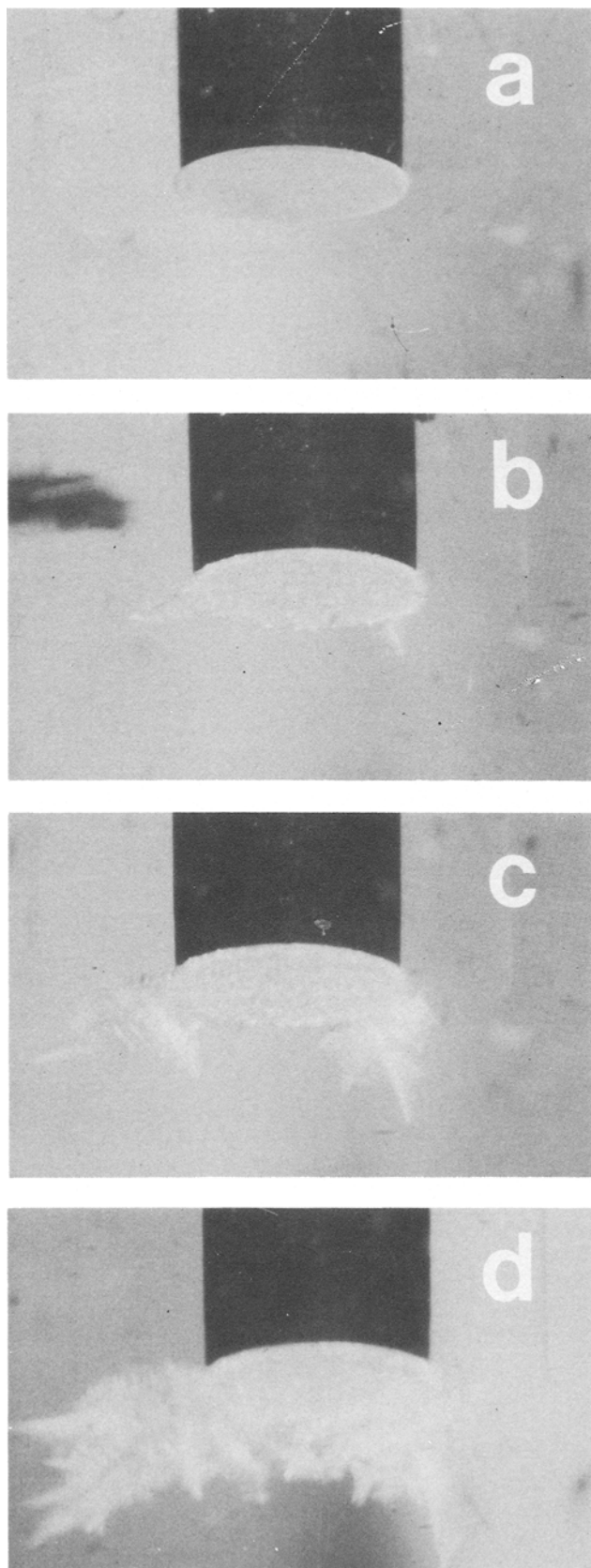*Electrochemical Society Active Member.

Fig. 3. Voltage-time curves for aluminum deposition at 30 mA/cm² and dendrite growth after deposition. (a) Prolonged deposition, dendrites appeared at (A) and large dendrites formed at (B). (b) Stopping deposition at (C) before dendrites appeared, dendrites appeared at (A) and large dendrites formed at (B). (c) Stopping deposition at (C) before dendrites appeared and starting anodization at (D): dendrites appeared at (A) and large dendrites formed at (B). (d) Stopping deposition at (C) before dendrites appeared and shaking the cell at (E): no dendrites formed at all.

Fig. 2. Dendrite growth after deposition at 57 mA/cm² for 8 min from NaAlCl₄ saturated with NaCl at 175°C. Diameter of carbon electrode: 3 mm. (a) At t = 0 when stopping deposition and opening the circuit. (b) At t = 18 min. (c) At t = 20 min. (d) At t = 21 min.

the electrolysis was stopped before dendrites were visible (at C) and a reversing current was applied to strip off the deposits (at D), dendrites still kept on growing during anodization and cell voltage remained negative until den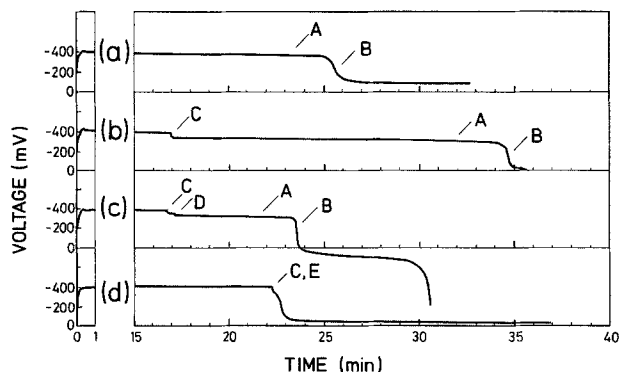drites were fully grown [at B, Fig. 3(c)]. It seems that dendrite growth will continue until full growth is attained no matter what happens: deposition, anodization, switching off current or open circuit in the period. However, short circuit seems to be able to stop the dendrite growth as long as the period of short circuit is long enough; otherwise, dendrites might appear anyway.

Figure 4 shows another example of aluminum dendrite growth after electrolysis at 70 mA/cm² for 6 min in an equimolar NaCl-AlCl₃ melt saturated with both NaCl and MnCl₂. The solubility of manganese chloride in NaAlCl₄ saturated with NaCl is found to be approximately 0.1 mole percent (m/o) at 175°C (6). Even such a small concentration of MnCl₂ had a pronounced effect on the morphology of the aluminum deposit (6). However, it had little influence on the electroless dendrite growth after the circuit was broken. Figure 4(a) shows the needlelike aluminum deposit at the moment when the electrolysis was stopped, t = 0. Figure 4(b) shows the appearance of the deposit at t = 4 min, i.e., 4 min after breaking the circuit. Dendrites appeared first at the top of the needlelike deposit. Figure 4(c) shows the situation at t = 8 min. Dendrites on the top of the needlelike deposit became more and more voluminous, and some small dendrites appeared in other regions of the deposit surface. Figure 4(d) shows the situation at t = 16 min. It is clear that the "electroless dendrite formation" is faster in this experiment than in the experiment shown in Fig. 2.

Discussion

In an attempt to understand the behavior of the dendritic growth and the voltage-time curves described above, we suggest that the concentration gradient of aluminum-containing species resulting from electrolysis might be the driving force for the electroless dendrite growth. The disproportionation of subvalent aluminum ions (7) is probably not responsible, because this situation seems to occur especially at high current density and high overvoltage dissolution on the anodic side.

During electrolysis, aluminum is deposited on the cathode through the discharge of aluminum-carrying ionic species (i.e., $AlCl_4^-$ in the present $NaAlCl_4$ melt saturated with NaCl) according to the following reaction (14, 15)

$$AlCl_4^- + 3e^- \rightarrow Al + 4Cl^- \qquad [1]$$
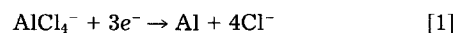
Thus the concentration of aluminum-carrying ions decreases in the vicinity of the cathode. Since the sodium ions transport the current to the cathode (16), the concentration of sodium ions there increases. The concentration overvoltage corresponds to the reversible cell potential of the following concentration cell
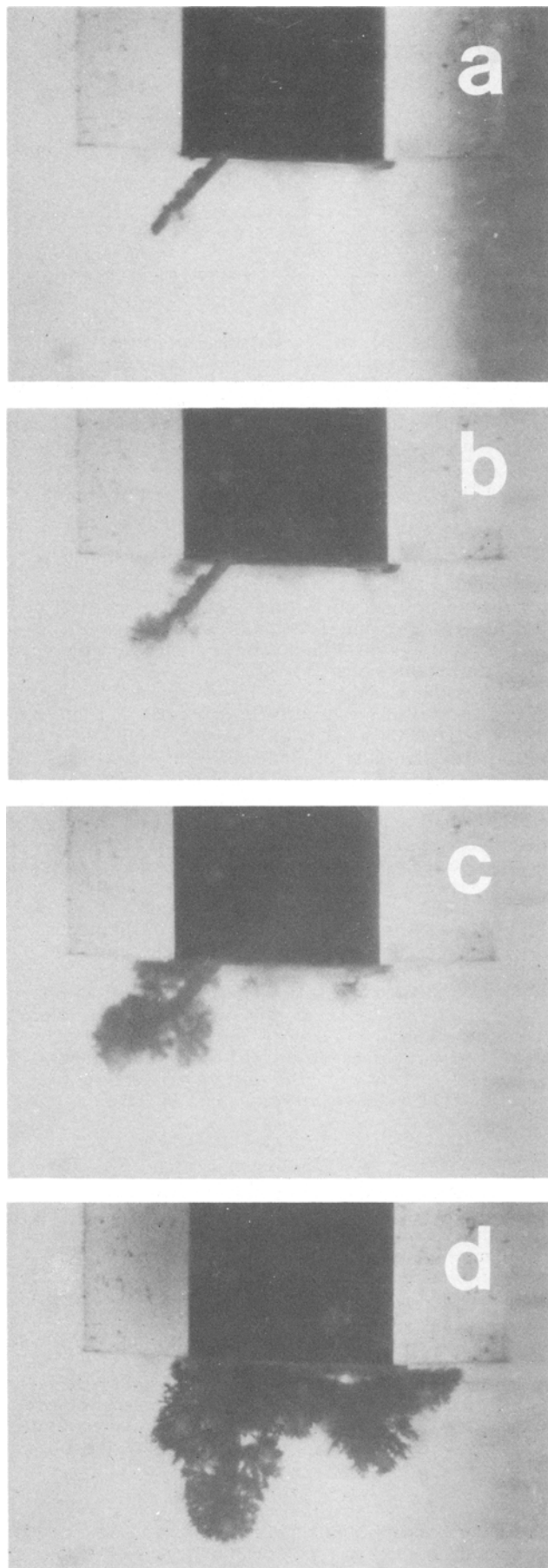
$$Al/NaCl\text{-}AlCl_{3(s)}/NaCl\text{-}AlCl_{3(b)}/Al$$

where subscripts (s) and (b) indicate the surface and bulk concentrations of both aluminum-containing species and sodium chloride, respectively. Such a cell should exhibit a cell potential corresponding to electrode reaction [1] such as (17)

$$E = \frac{RT}{3\mathbf{F}} \ln \left\{ \frac{(AlCl_4^-)_{(b)}(Cl^-)_{(s)}^4}{(AlCl_4^-)_{(s)}(Cl^-)_{(b)}^4} \right\} \qquad [2]$$

If there are any protrusions, for example in the form of needlelike aluminum deposits on the surface of the cathode (see Fig. 5), which to some extent penetrate through the concentration gradient, the situation is actually the same as a short circuit between the two electrodes in the above-mentioned concentration cell. In such a cell, aluminum is plated on the electrode in the AlCl$_3$-rich chamber and dissolved from the electrode in the less-rich aluminum chloride chamber, *i.e.*, in the present case, aluminum dissolves from the basis and deposits onto the top of the needlelike deposit. In the case where no visible protrusion exists, as shown in Fig. 2a, dendritic growth is very slow in the initial stage, when the difference in concentrations is small between the top and basis of small protrusive dendrites. As soon as a noticeable dendrite is formed, the procedure of dendrite growth becomes very fast, because of the large concentration gradient. This explains why the delay time is shorter for the experiment shown in Fig. 4 than that for the experiment shown in Fig. 2. When mature dendrites are formed, the concentration gradient can be totally eliminated, and therefore the excessive high overvoltage disappears soon, as seen in Fig. 3.

Shaking the cell.—In order to demonstrate the above assumption, two sets of deposition experiments were carried out in the same way. After deposition one of the cells was vigorously shaken to eliminate the concentration gradient while the other cell was kept undisturbed. It was found that the voltage dropped down from the higher value [Fig. 3(d)] as soon as the vigorous shaking occurred, and the dendrite growth could be inhibited completely in the shaken cell, whereas the dendrite growth still occurred in the other cell. If the source of aluminum was subvalent ions Al$^+$, the shaking should not prevent the dendrite growth.

Short-circuiting the concentration cell.—A two-chamber cell was used of the type described previously (18) but with aluminum electrodes instead of carbon electrodes placed in each chamber separately. The two chambers were filled with acidic eutectic (*ca.* 63.7 m/o AlCl$_3$) and equimolar (*ca.* 50 m/o AlCl$_3$) sodium aluminum chloride, respectively. The voltage between the two aluminum electrodes was *ca.* 410 mV. The two electrodes were then short-circuited. During several hours of short-circuiting, aluminum dendrites grew on the aluminum electrode in the AlCl$_3$-rich chamber. It is clear that the driving force for aluminum deposition in this case is the difference in the AlCl$_3$ con-

Fig. 4. Dendrite growth after deposition at 70 mA/cm^2 for 6 min from an equimolar NaCl-AlCl$_3$ melt saturated with both NaCl and MnCl$_2$ (*ca.* 0.4 and 0.1 m/o, respectively) at 175°C. Diameter of carbon electrode: 3 mm. (a) At $t = 0$ when stopping deposition and opening the circuit. (b) At $t = 4$ min. (c) At $t = 8$ min. (d) At $t = 16$ min.
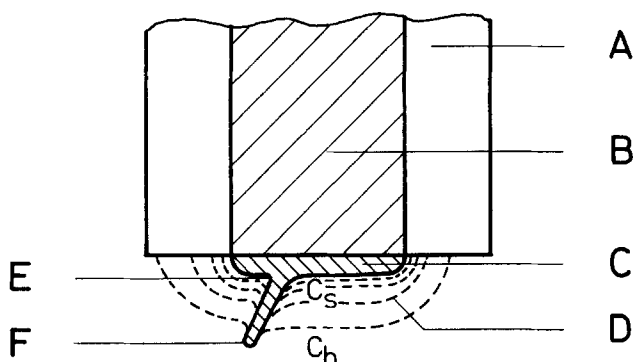
Fig. 5. Illustration of concentration cell formed in case of dendritic protrusions: A, glass covering; B, glassy carbon electrode; C, aluminum deposits; D, isoconcentration lines; E, the base of needlelike deposits where Al dissolves; F, the top of needlelike deposits where Al deposits; C$_s$, surface concentration; and C$_b$, bulk concentration.
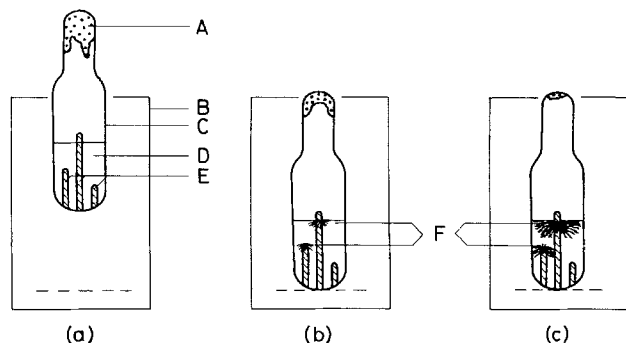
Fig. 6. Schematic representation of apparatus for aluminum dendrite growth in 36.3 m/o NaCl-63.7 m/o AlCl₃ melt: (a) first stage for partial AlCl₃ vaporization; (b) and (c) aluminum dendrite growth during AlCl₃ dissolving. A, aluminum chloride crystals; B, furnace; C, cell wall; D, melt; E, aluminum pieces; and F, aluminum dendrites formed.

centrations between the two chambers. It is less clear how much the formation of a local gradient set up during the short-circuiting contributed to the dendrite formation.

Re-examination of "aluminum recrystallization."—In his research for a new aluminum refining technique at lower temperatures, Midorikawa (19) found that aluminum could be recrystallized from aluminum chloride baths when the concentration of aluminum chloride was changed. It was explained as aluminum dissolving in the melt to form some subvalent aluminum (I) ions which, upon addition of AlCl₃, disproportionated to produce aluminum metal. Notoya (20) reported a similar phenomenon, and pointed out that the temperature difference and/or concentration difference of Al(III), apart from subvalent ions of aluminum, might be the cause of the recrystallization. The experimental procedure described by Midorikawa was repeated and confirmed in this laboratory. The schematic representation of the apparatus is shown in Fig. 6.

The premixed 36.3 m/o NaCl-63.7 m/o AlCl₃ salts were contained in a sealed cell with three pieces of aluminum metal of different lengths. At the first stage of the experiment, the top part of the cell was kept out of the furnace while the temperature of the bottom part of the cell was controlled at 175°C. Aluminum chloride vaporized and condensed on the inside wall of the top part of the cell, as shown in Fig. 6(a). Thereafter the whole cell was moved down into the furnace. In this way the aluminum chloride crystals were heated and slowly fused into the bath below, resulting in a higher concentration of aluminum-carrying species in the top layer than in the bottom layer of the bath. During this procedure, many dendritic aluminum crystals were formed on the top of the long piece of aluminum, and fewer were formed on the top of the aluminum piece of middle length, whereas no aluminum dendrite formed on the short piece of aluminum, as shown in Fig. 6(b) and (c).

Hence, all evidence seems to support the assumption that the concentration gradient of AlCl₃ resulting from electrolysis is the cause for aluminum dendrite growth after deposition. In the kinetic theory (21-22) of dendrite formation in metal electrodeposition, only the roles of diffusion and nucleation processes were emphasized. It therefore seems correct to deduce from the present study that the concentration gradient, besides diffusion and nucleation, is another factor which can cause dendrite growth.

Conclusion

Aluminum deposits in NaCl-AlCl₃ melt are found to be unstable, and dendrites continue to grow after the initial electrodeposition unless the electrolyte is shaken. The electroless growth process of aluminum dendrites has been examined and explained. The difference in the concentrations of aluminum chloride, resulting from the deposition process, in the vicinity of the cathode surface constitutes a type of concentration cell. The short-circuited discharging of this concentration cell can drive the growth of aluminum dendrites. It should be noted that this phenomenon may also be present during normal metal deposition, and in this way give rise to an extra dendrite growth.

Acknowledgments

REFERENCES

1. H. A. Hjuler, R. W. Berg, and N. J. Bjerrum, *Power Sources*, **10**, 1 (1985).
2. B. Nayak and M. M. Misra, *J. Appl. Electrochem.*, **9**, 699 (1979).
3. K. Grjotheim and K. Matiašovský, *Acta. Chem. Scand.*, **A34**, 666 (1980).
4. M. Chrenkova-Paucirova, P. Fellner, A. Silný, and K. Matiašovský, *Surface Techn.*, **16**, 15 (1982).
5. Yu. K. Delimarsky and N. K. Tumanova, *Electrochim. Acta*, **24**, 19 (1979).
6. Li Qingfeng, H. A. Hjuler, R. W. Berg, and N. J. Bjerrum, *This Journal*, To be published.
7. Yu. K. Delimarsky, V. F. Makogon, and A. Ya. Zhigailo, *Sov. Electrochem.*, **5**, 98 (1969).
8. R. J. Gale and R. A. Osteryoung, *This Journal*, **121**, 983 (1974).
9. J. Robinson and R. A. Osteryoung, *ibid.*, **127**, 122 (1980).
10. P. K. Lai and M. Skyllas-Kazacos, *Electrochim. Acta.*, **32**, 1443 (1987).
11. Qi-Xian Qin and M. Skyllas-Kazacos, *J. Electroanal. Chem.*, **168**, 193 (1984).
12. R. W. Berg, H. A. Hjuler, and N. J. Bjerrum, *Inorg. Chem.*, **23**, 557 (1984).
13. S. von Winbush, H. A. Hjuler, R. W. Berg, and N. J. Bjerrum, *This Journal*, **136**, 901 (1989).
14. B. Trémillon and G. Letisse, *J. Electroanal. Chem.*, **17**, 371 (1968).
15. Y. Chryssoulakis, J-C. Poignet, and G. Manoli, *J. Appl. Electrochem.*, **17**, 857 (1987).
16. C. L. Hussey and H. A. Øye, *This Journal*, **131**, 1621 (1984).
17. L. G. Boxall, H. L. Jones, and R. A. Osteryoung, *ibid.*, **120**, 223 (1973).
18. J. H. von Barner and N. J. Bjerrum, *Inorg. Chem.*, **12**, 1891 (1973).
19. R. Midorikawa, *Denki Kagaku*, **25**, 13 (1957).
20. T. Notoya, *Electrochim. Acta*, **13**, 2194 (1968).
21. A. R. Despić and K. I. Popov, in "Modern Aspects of Electrochemistry," No. 7, B. E. Conway and J. O'M. Bockris, Editors, Ch. 4, p. 199, Butterworths, London (1972).
22. A. R. Despić, in "Comprehensive Treatise of Electrochemistry," Vol. 7, B. E. Conway, J. O'M. Bockris, E. Yeager, S. U. M. Khan, and R. E. White, Editors, Ch. 7B, p. 451, Plenum Press, New York (1983).