

# The corrosion and electrochemical behaviour of pure aluminium in alkaline methanol solutions

Jun-Bo Wang · Jian-Ming Wang · Hai-Bo Shao ·  
Jian-Qing Zhang · Chu-Nan Cao

Received: 6 September 2006 / Accepted: 8 February 2007 / Published online: 7 March 2007  
© Springer Science+Business Media B.V. 2007

**Abstract** The corrosion and electrochemical behaviour of pure aluminium in alkaline methanol solutions has been investigated. The results of hydrogen collection experiments showed that aluminium has a lower corrosion rate in alkaline methanol solutions compared to water based solutions and that the corrosion rate increases with increasing water content of the solution. Polarization and galvanostatic discharge experiments showed that there is a wide potential window of electrochemical activity and a better discharge performance in the alkaline methanol solutions with a certain amount of water. Scanning electron microscopy (SEM) and energy dispersive analysis of X-ray (EDAX) showed that the passivation in the later stages of discharge in alkaline methanol solutions at relatively high current densities is due to the formation of a dense  $\text{Al}(\text{OH})_3$  layer on the surface of the anode.

**Keywords** Pure aluminium · Alkaline methanol solution · Corrosion · Electrochemical behaviour

## 1 Introduction

Aluminium is an abundant, attractive anode material for energy storage and conversion because of its high

specific capacity, very negative standard electrode potential and environmentally benign characteristics. Compared with zinc, lithium and other metals, aluminium has its own unique advantages and disadvantages. The physical and chemical properties of aluminium in combination with its almost unlimited reserves explain the considerable interest shown in aluminium as an anode material for batteries [1].

Much attention has been paid to the use of aluminium as an anode material in batteries using saline [2], alkaline [3–5] and non-aqueous [6] electrolyte systems. However, up to now, aluminium has not been a successful commercial energy providing material, and only a few types of aluminium batteries have been industrially produced. This is because aluminium also exhibits some less attractive properties, such as high self-corrosion rate with hydrogen evolution in the alkaline solutions both at open-circuit conditions and during the discharge process. This wasteful self-corrosion results in unacceptably high-energy losses during standby. Moreover, significant potential is lost during cell discharge due to the presence of the spontaneously formed passive film on the surface of aluminium. In aqueous and non-aqueous saline systems the passive film makes the potential of the anode much more positive than the theoretical value. Of course, the surface film can be removed by strong acid or alkaline aqueous electrolytes. However, in such media aluminium undergoes serious self-discharge. In order to reduce the self-corrosion of the aluminium anode, two methods are usually used: either (1) alloying aluminium with other elements [7–13] and/or (2) modifying the composition of electrolyte [14–20]. A successful system must keep the aluminium anode active whilst reducing the corrosion rate to a low level.

J.-B. Wang · J.-M. Wang (✉) · H.-B. Shao ·  
J.-Q. Zhang · C.-N. Cao  
Department of Chemistry, Zhejiang University, Hangzhou  
310027, P.R. China  
e-mail: wjm@cmsce.zju.edu.cn

J.-Q. Zhang · C.-N. Cao  
Chinese State Key Laboratory for Corrosion and Protection,  
Shenyang 110015, P.R. China

In this work, the electrochemical behaviour of pure aluminium has been investigated in a new electrolyte system based on potassium hydroxide methanol solutions as the electrolyte. In this medium, aluminium is electrochemically active due to the use of the alkali, and hydrogen evolution can be inhibited because of the substitution of methanol for solvent water.

## 2 Experimental

### 2.1 Electrochemical measurements

Electrochemical measurements were carried out in a classical three-electrode glass cell. The working electrode was made of pure aluminium (supplied by Johnson Matthey, purity no less than 99.9995%) in the form of 6 mm in diameter rods. The electrode was insulated with epoxy resin except for the surface to be tested. Before each test the electrode surface was polished by 2,000 grit waterproof abrasive paper, degreased in acetone and rinsed in deionized water. The counter electrode was a platinum foil and the reference electrode a Hg/HgO electrode. All the solutions were prepared by reagents of AR grade and deionized water, and they were purged with nitrogen to remove oxygen before measurements were made.

The measurement system used a potentiostat/galvanostat (EG&G model 273A), controlled by a micro-computer. The potentiodynamic polarization curves were measured at a scanning rate of 1 mV s<sup>-1</sup>, and galvanostatic discharge was performed at different current densities. All the electrochemical experiments were conducted at a constant temperature of 25 °C.

### 2.2 Determination of corrosion rates

Corrosion rates were determined by a hydrogen collection method. The apparatus used was as described elsewhere [7]. The electrode was made of the same aluminium rod as that used in the electrochemical experiments, with a surface area of 0.284 cm<sup>2</sup>. Before each test the electrode surface was degreased in acetone and rinsed in de-ionized water, and the solutions used were purged with nitrogen to remove oxygen. The corrosion current density ( $I_{\text{corr}}$ ) of aluminium electrode was calculated as follows:

$$I_{\text{corr}} = \frac{2pVF}{tSRT} \quad (1)$$

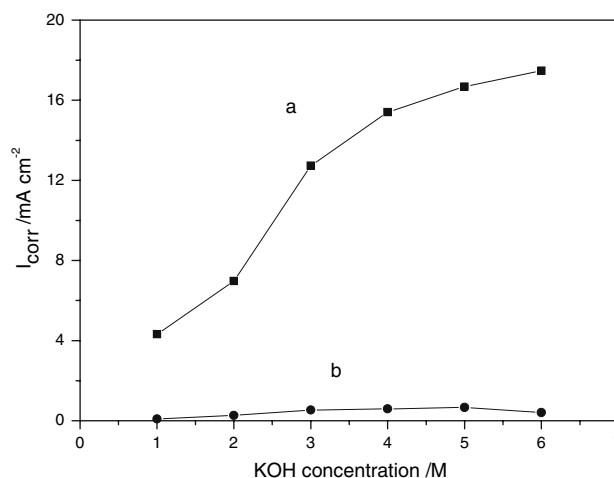
where  $p$  is atmospheric pressure,  $S$  electrode area,  $t$  collecting time, and other parameters have their usual meanings.

### 2.3 Surface characterization

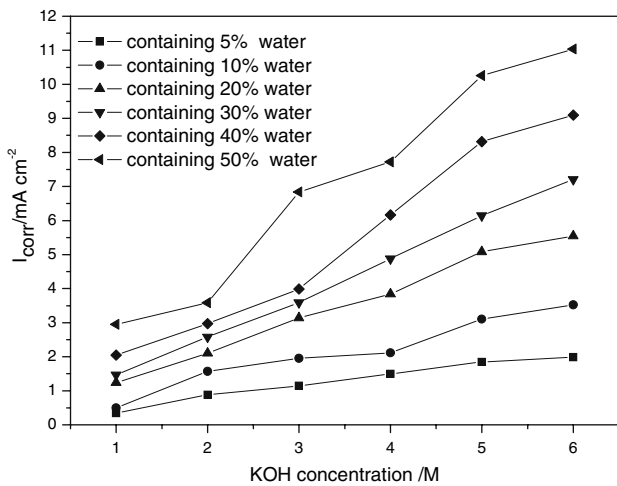
The morphologies of the aluminium anodes were examined by a Philips model XL30 scanning electron microscope (SEM). The composition of the product layer on aluminium anodes was analyzed by energy dispersive analysis of X-ray (EDAX) (GENE IS 4000).

## 3 Results and discussion

Figure 1 shows the corrosion behaviour of aluminium in aqueous and anhydrous methanol based KOH solutions of increasing concentration. It can be seen that generally the corrosion current density of aluminium in both aqueous solutions and anhydrous methanol solutions of KOH increases with increasing KOH concentration. This is because higher alkaline concentration can enhance the electrochemical activity of aluminium. The slight decrease in corrosion current density in the 6 M KOH methanol solution may be caused by the higher viscosity of the solution. The corrosion rate of aluminium in anhydrous KOH methanol solutions is reduced and is less than 5% of that in the corresponding concentration aqueous solution. Figure 2 shows that the corrosion rate of aluminium increases with progressive increase in water and KOH contents in the methanol solutions.



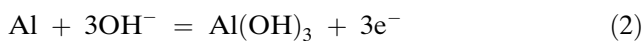
**Fig. 1** Corrosion current densities of aluminium in aqueous solutions (a) and anhydrous methanol solutions (b) with various KOH concentrations



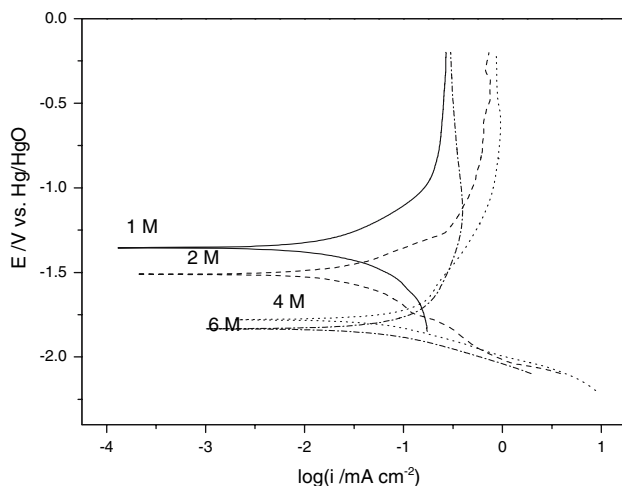
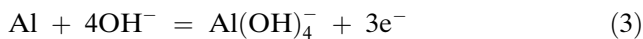
**Fig. 2** Effects of water content on the corrosion current densities of aluminium in methanol solutions with various KOH concentrations

Polarization measurements were carried out to investigate the electrochemical behaviour of aluminium in anhydrous KOH methanol solutions, and the results are presented in Fig. 3. The anodic reaction is the dissolution of aluminium and the dominant cathodic reaction is the reduction of solvent water or methanol [21–24]. The corresponding electrode reactions are as follows:

Anode reaction:

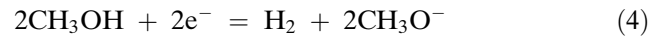


or



**Fig. 3** Polarization curves of aluminium in anhydrous methanol solutions with various KOH concentrations

Cathode reaction:

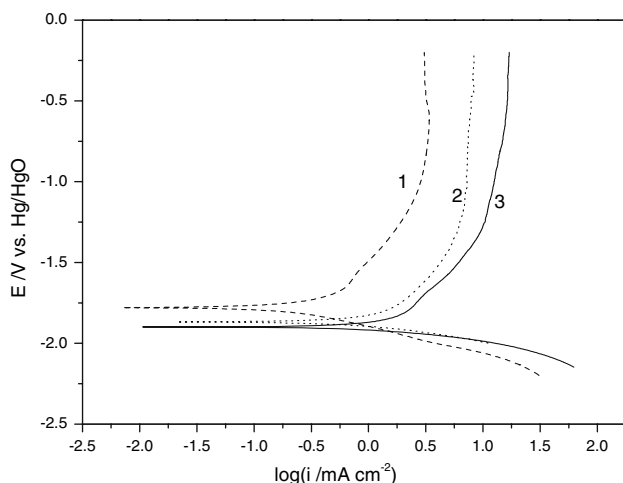


or

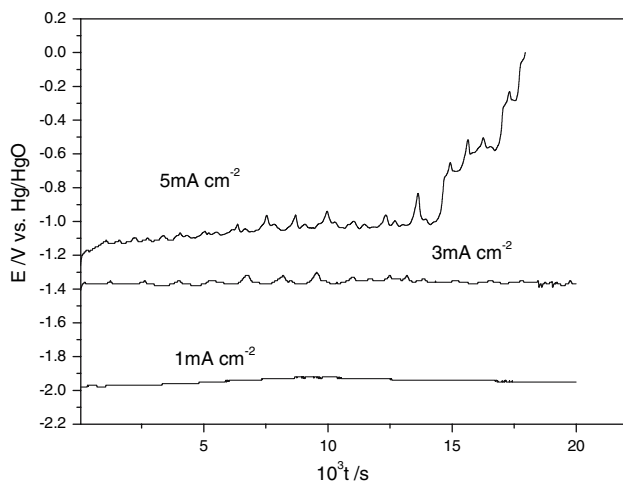


It can be seen from Fig. 3 that the cathodic portion of the polarization curves is generally independent of KOH concentration. This is reasonable because the cathodic reaction is mainly the reduction of methanol and its activity is almost constant in anhydrous methanol solutions. In the anodic portion an almost constant potential-independent current density is achieved at relatively positive potentials. This behaviour can be explained in terms of the dissolution of aluminium through a porous product layer that permits charge transfer and ionic conduction [23–24]. In this range of potential aluminium may be considered to be in a pseudo-passivation state. As the KOH concentration in the anhydrous methanol solutions increases, the product layer on the surface of aluminium becomes thinner and this leads to the general increase in the potential-independent anodic current density and the shift of the open-circuit potential (OCP) in the negative direction. The lower potential-independent anodic current density of aluminium in the anhydrous methanol solution with 6 M KOH may, as before, result from the high viscosity of the solution. The trend of the potential-independent anodic current density with change in KOH concentration in the anhydrous methanol solutions is consistent with that of the corresponding corrosion rate. Aluminium is electrochemically active over a very wide potential window and the highest anodic current density is achieved in the 4 M KOH methanol solution. Figure 4 shows that both the anodic and cathodic current densities can be significantly increased by the addition of water in 4 M KOH methanol solutions. The hydration of the surface product layer [25] improves the anodic dissolution of aluminium and the reduction reaction of water [reaction (5)] may have a considerable contribution to the cathodic current density. The conductivity of the electrolyte generally rises with the increase in water and KOH contents in methanol solutions [19] and this may be partially responsible for the increase in anodic and cathodic current densities. The results of the above polarization measurements are in agreement with those of hydrogen collection experiments.

Figure 5 shows the galvanostatic discharge curves of aluminium in 4 M KOH anhydrous methanol solutions. The aluminium anodes have a very flat

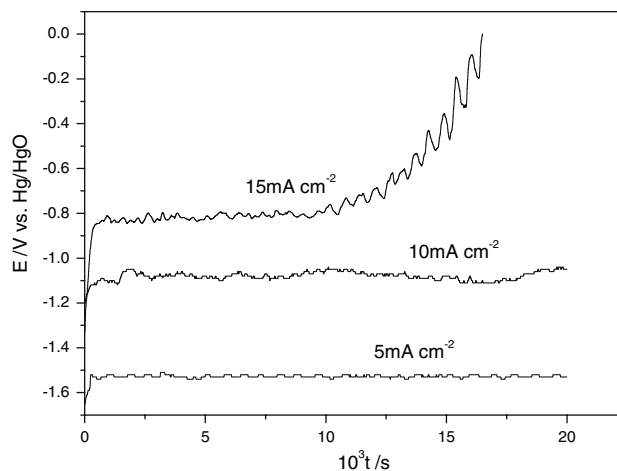


**Fig. 4** Polarization curves of aluminium in 4 M KOH methanol solutions with various water contents. (1) free of water; (2) 10% water (3) 20% water

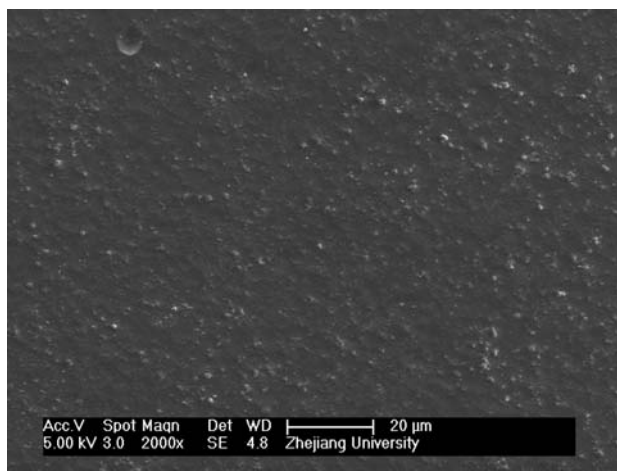


**Fig. 5** Galvanostatic discharge curves of pure aluminium in 4 M KOH anhydrous methanol solutions at various current densities

discharge plateau at relatively low potentials. With increasing discharge current density the electrode polarization increases and then the discharge potential moves in the positive direction. The rapid potential increase of the anode after having been discharged for about 4 h at  $5 \text{ mA cm}^{-2}$  implies that the anode has become passive. Figure 6 shows that in the 4 M KOH methanol solution with 20% water the anode can discharge stably at higher current densities ( $\leq 10 \text{ mA cm}^{-2}$ ) at potentials that are more negative than those in the anhydrous solution system at the same discharge current density. This demonstrates that the discharge of aluminium is improved by the addition of  $\text{H}_2\text{O}$  to the 4 M KOH anhydrous meth-



**Fig. 6** Galvanostatic discharge curves of pure aluminium in the 4 M KOH methanol solutions containing 20% water at various current densities

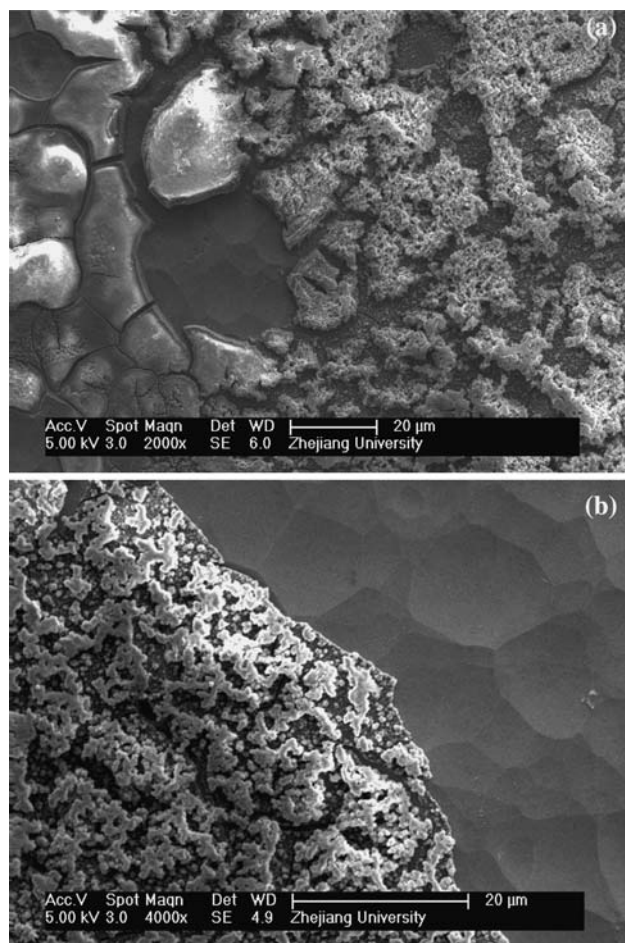


**Fig. 7** SEM image of the aluminium anode after being discharged in the 4 M KOH methanol solution with 20% water at  $5 \text{ mA cm}^{-2}$

anol solution. However, passivation of the anode also occurs after being discharged for about 3 h at a current density of  $15 \text{ mA cm}^{-2}$ . It can also be seen from Figs. 5 and 6 that potential fluctuation occurs on the discharge curves and the amplitude increases with increasing discharge current density. This may result from the formation and peeling away of the product layer on the aluminium surface.

SEM imaging of the discharged anodes (Figs. 7 and 8) showed less corrosion products on the surface of the anode discharged in the 4 M KOH methanol solution with 20% water at  $5 \text{ mA cm}^{-2}$  compared to the anode discharged at  $15 \text{ mA cm}^{-2}$  where its surface was covered by a thick product layer (Fig. 8a). The surface layer





**Fig. 8** SEM image of the aluminium anode after being discharged in the 4 M KOH methanol solution with 20% water at  $15 \text{ mA cm}^{-2}$ . **(a)** One part of aluminium surface completely covered with surface layer; **(b)** The surface after peeling off one part of surface layer

consists of a loose and porous outer layer and a dense inside layer that may impede the mass transfer of reactive species and this may be responsible for the rapid potential increase in the later stage of aluminium anode discharge at higher current densities [21]. The EDAX results (Table 1) show that the molar ratio of aluminium and oxygen in the surface product is approximately 1:3, suggesting that the surface product on the discharged aluminium anode is mainly  $\text{Al}(\text{OH})_3$  [24]. The discharge of an aluminium anode at relatively higher current

**Table 1** The elemental composition\* of the product layer on the surface of the anode discharged at  $15 \text{ mA cm}^{-2}$

Element	Atomic percentage (%)
Al	74.75
O	24.31
K	0.94

\* Element H is not included

densities can result in an enrichment of aluminate ions  $\text{Al}(\text{OH})_4^-$  in the electrolyte as well as a decrease in the alkalinity of the electrode interface. These two factors make a considerable contribution to the stabilization of the  $\text{Al}(\text{OH})_3$  passivating species at the surface. As the discharge process progresses the  $\text{Al}(\text{OH})_3$  surface layer becomes thicker and denser and this finally leads to severe passivation. The formation of the dense  $\text{Al}(\text{OH})_3$  surface layer must be inhibited to improve the discharge performance. This may be achieved using additives to the electrolyte or aluminium [1]. The experimental results also imply that an anode with a high specific surface area (e.g. aluminium powder) may show better discharge performance.

#### 4 Conclusions

- (1) The corrosion of aluminium in KOH methanol solutions is significantly inhibited. Although, the corrosion rate of aluminium increases with increasing water content in KOH methanol solutions, it is still low when the content of water is less than 20%.
- (2) In KOH methanol solutions aluminium is electrochemically active over a wide potential window, and displays a very flat discharge plateau. The addition of water to the KOH methanol solutions improves the anode performance.
- (3) The rapid potential increase in the later stages of discharge at relatively high current densities may result from the formation of a dense  $\text{Al}(\text{OH})_3$  layer on the aluminum anode surface.

**Acknowledgements** This work was supported by National Natural Science Foundation of China (approved No. 50571091). The authors also gratefully acknowledge financial support of the Chinese State Key Laboratory for Corrosion and Protection.

#### References

1. Li QF, Bjerrum NJ (2002) *J. Power Sources* 110:1
2. Venugopal A, Raja VS (1997) *Corros Sci* 39:1285
3. Emregül KC, Aksüt AA (2000) *Corros Sci* 42:2051
4. Moon SM, Pyun SI (1999) *Electrochim Acta* 44:2445
5. Armstrong RD, Braham VJ (1996) *Corros Sci* 38:1463
6. Rybalka KV, Beketaeva LA (1993) *J Power Sources* 42:377
7. Abedin SZE, Saleh AO (2004) *J Appl Electrochem* 34:331
8. Macdonald DD, Lee KH, Mocarri A, Harrington D (1988) *Corrosion* 44:652
9. Krishnan M, Subramanyan N (1977) *Corros Sci* 17:893
10. Paramasivam M, Iyer SV (2001) *J Appl Electrochem* 31:115
11. Scamans G, Hunter J, Tuck CDS, Hamlen R, Fitzpatrick N (1989) *J Power Sources* 12:363

12. Shayeb HAE, Abd El Wahab FM, Abedin SZE (1999) *J Appl Electrochem* 29:473
13. Paramasivam M, Jayachandran M, Iyer SV (2003) *J Appl Electrochem* 33:303
14. Wang XY, Wang JM, Shao HB, Zhang JQ, Cao CN (2005) *J Appl Electrochem* 35:213
15. Macdonald DD, English C (1990) *J Appl Electrochem* 20:405
16. Shao HB, Wang JM, Zhang Z, Zhang JQ, Cao CN (2002) *Mater Chem Phys* 77:305
17. Ein-Eli Y, Auinat M, Starosvetsky D (2003) *J Power Sources* 114:330
18. Maayta AK, Al-Rawashdeh NAF (2004) *Corros Sci* 46:1129
19. Mukherjee A, Basumallick IN (1996) *J Power Sources* 58:183
20. Kapali V, Iyer SV, Balaramachandran V, Sarangapani KB, Ganesan M, Kulandainathan MA, Mideen AS (1992) *J Power Sources* 39:263
21. Macdonald DD, Real S, Smedley SI, Urquidi-Macdonald M (1988) *J Electrochem Soc* 135:2410
22. Shao HB, Wang JM, Zhang Z, Zhang JQ, Cao CN (2003) *J Electroanal Chem* 549:145
23. Brown OR, Whitley JS (1987) *Electrochim Acta* 32:545
24. Doche ML, Rameau JJ, Durand R, Novel-Cattin F (1999) *Corros Sci* 41:805
25. Shao HB, Wang JM, Wang XY, Zhang JQ, Cao CN (2004) *Electrochem Commun* 6:6