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DEVELOPMENT OF NEW ALLOYS OF COMMERCIAL ALUMINIUM (2S) WITH ZINC, INDIUM, TIN, AND BISMUTH AS ANODES FOR ALKALINE BATTERIES

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Summary

Studies show that the addition of zinc to commercial aluminium increases both the corrosion rate and the open-circuit potential (OCP) in alkaline medium. The addition of indium gives rise to a ternary alloy that shows a slightly higher OCP and an appreciably reduced extent of self corrosion. Addition of bismuth results in a quaternary alloy whose corrosion rate is comparable with the ternary alloy, but the OCP is found to be higher. Anodic polarisation characteristics and anode efficiency are found to be in favour of quaternary alloys. Electrochemical studies with Al, Zn, Sn ternary alloys and Al, Zn, Sn, Bi quaternary alloy favours the choice of the latter as a galvanic anode. Among the two types of quaternary alloys, those containing indium, rather than tin, are found to be more suitable as alkaline battery anodes.

Introduction

India is one of the countries where the production of aluminium has reached self sufficiency and shortly there may be a surplus. One of the possible uses of aluminium is in the development of aluminium alloys for the preparation of anodes for alkaline batteries in combination with porous carbon cathodes. Aluminium has certain unique properties such as a high energy density and a high negative potential in alkaline media [1 - 5]. Unfortunately, however, it corrodes heavily in alkaline electrolytes.

A solution based on 4 M NaOH containing 20% sodium citrate and 0.4% CaO has been developed as an aluminium/air battery electrolyte in CECRI with aluminium (2S) (99% pure) as the anode material and porous carbon as the cathode [6 - 9]. Recently, different grades of aluminium, such

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as spec. pure (99.9999%), electrolytic (99.5 - 99.7%) and commercial, were tested for their utility as a galvanic anode in 4 M NaOH solution containing CaO and sodium citrate [6]. Different grades of commercial aluminium, namely, 2S, 3S, 26S and 57S were also examined as galvanic anodes in 1 M NaOH solution containing CaO and sodium citrate [10]. The performance of a few binary alloys of aluminium was assessed by adding different percentages of indium, gallium, and thallium [5, 7, 11 - 13]. Sarangapani *et al.* [14] have observed that the addition of indium to aluminium could lead to a suitable alloy for use in alkaline batteries. In the present study, the effect of the addition of bismuth on an alloy of commercial aluminium with zinc, indium, and tin has been examined in alkaline media.

Development of aluminium-based alloy anodes for alkaline/air batteries is being carried out intensively in a number of laboratories throughout the world. But in all these investigations only 99.99%- or 99.999%-pure aluminium is being used as the starting material [1 - 5]. In India, however, 99.99%-pure aluminium is not manufactured by any of the firms connected with aluminium production. In fact, it was only recently that M/s NALCO, Orissa, announced the possibility of producing 99.8%-pure aluminium; this would be the most pure aluminium available in India. Hence, it was felt that the research work should be aimed at studying the utility of less-pure grades of aluminium in alloys for use in aluminium/air batteries. A good anode should be selected on the basis of: (i) a high negative open-circuit potential; (ii) low corrosion rate; (iii) low anodic polarisation; (iv) high efficiency.

Experimental

Materials

Self-corrosion studies were conducted on rectangular metal strips of size 5 cm × 2 cm. Cylindrical rod specimens of cross-sectional area (5.02 cm^2) were used for polarisation, open-circuit potential (OCP) and anode efficiency measurements. All specimens were cloth buffed in the presence of pumice and then degreased with trichloroethylene before use.

Chemicals

Sodium hydroxide and sodium citrate were of L.R. grade (M/s Ranbaxy Laboratories Ltd.). High purity calcium oxide (Merck) was used after prolonged heating to decompose any $CaCO_3$ contained in the sample. All solutions were prepared in distilled water.

Procedure

Corrosion rate measurements

Corrosion rates were determined by weight-loss measurements over a known duration. Metal specimens (triplicate) were polished by cloth buffing, degreased with trichloroethylene, and then weighed. The weighed specimens were immersed in 200 ml of electrolyte consisting of 20% sodium citrate + 4 M NaOH + 0.4% CaO. After 30 min, the specimens were removed, thoroughly washed with tap water, then with distilled water, dried, weighed, and the respective weight losses calculated.

Open-circuit potential measurement

The steady state OCP of specimens was measured using an Hg/HgO/4 M NaOH reference electrode. Note, all potentials in this paper are reported with regard to this electrode. For this experiment, cylindrical rod specimens were used. When the electrode potential reached a steady value, it was taken as the OCP of the specimen.

Anodic and cathodic polarisation

Anodic and cathodic polarisation studies were carried out at different current densities, from zero to 150 mA cm^{-2}, on cylindrical, rod-shaped specimens (5.02 cm^2 area). The counter and reference electrodes were of platinum gauze and Hg/HgO/4 M NaOH, respectively. The electrolyte solution was stirred throughout the experiment. Figures 1 - 4 show plots of

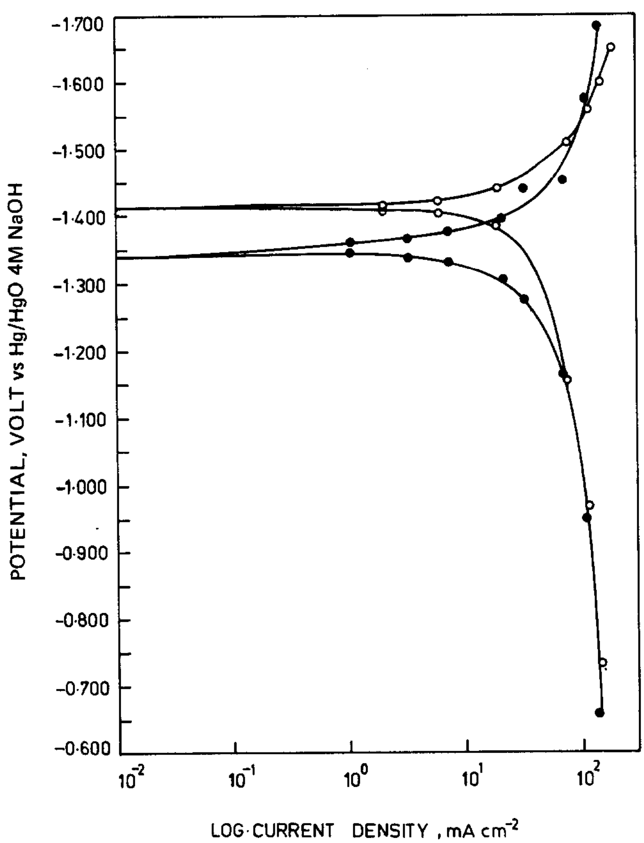


Fig. 1. Galvanostatic polarisation of commercial aluminium (2S) and its alloys in 4 M NaOH–20% sodium citrate–0.4% CaO electrolyte. ●, Al(2S); ○, Al(2S)–4%Zn.

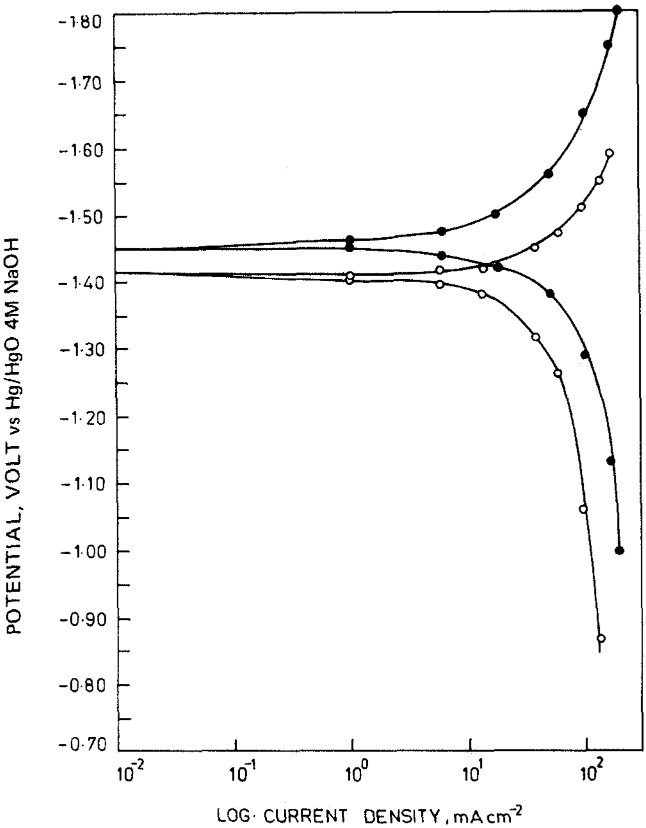
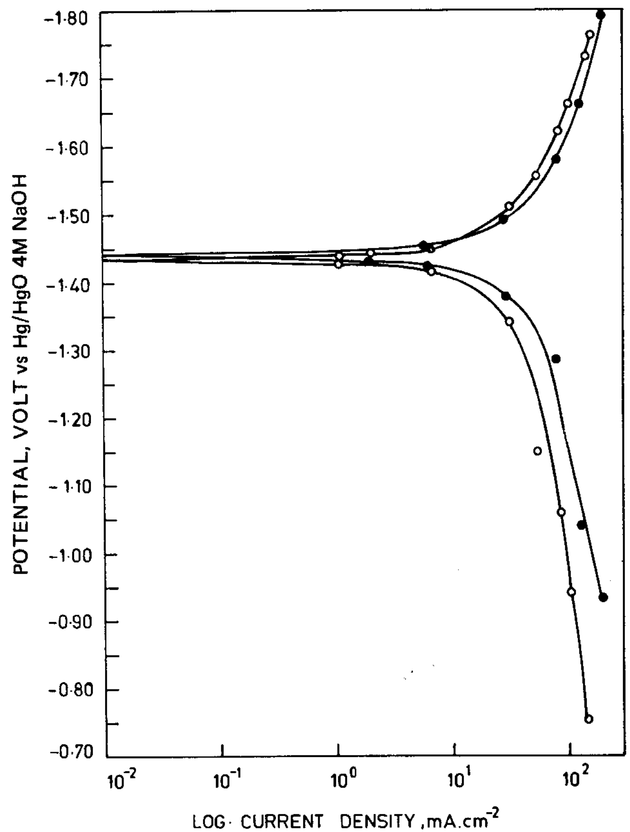


Fig. 2. Galvanostatic polarisation of commercial aluminium (2S) and its alloys in 4 M NaOH–20% sodium citrate–0.4% CaO electrolyte. ○, Al(2S)–4%Zn–0.025%In; ●, Al(2S)–4%Zn–0.025%In–0.1%Bi.

potential *versus* log{current density}. From these data, it is clear that corrosion of aluminium (2S) and its binary, ternary and quaternary alloys with Zn, In, Sn, and Bi in alkaline citrate solution is under anodic control.

Anode efficiency

The anode efficiency (%) was obtained at different current densities, namely, 25, 50, 75, 100, 125 and 150 mA cm^{-2}. Specimens were of cylindrical rod shape (exposed area 5.02 cm^2) and a platinum gauze was used as the counter electrode. The specimen was degreased and weighed before introduction into the electrolyte solution. Using a galvanostat, a given current density was impressed on the electrode for 2 h. At the end of the experiment, the specimen was removed and the weight loss was determined. The anode efficiency was calculated using the relation:



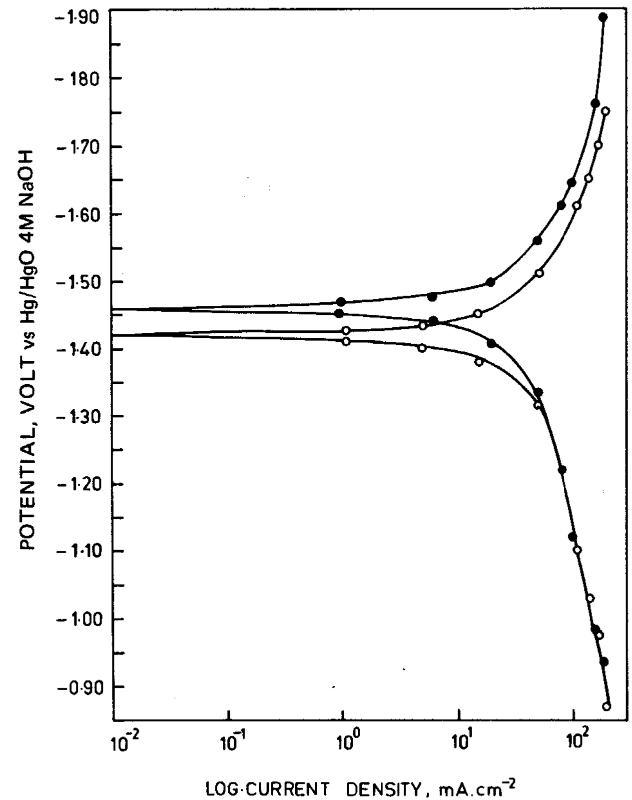


Fig. 3. Galvanostatic polarisation of commercial aluminium (2S) and its alloys in 4 M NaOH–20% sodium citrate–0.4% CaO electrolyte. ○, Al(2S)–4%Zn–0.05%In; ●, Al(2S)–4%Zn–0.05%In–0.5%Bi.

Fig. 4. Galvanostatic polarisation of commercial aluminium (2S) and its alloys in 4 M NaOH–20% sodium citrate–0.4% CaO electrolyte. ○, Al(2S)–4%Zn–0.25%Sn; ●, Al(2S)–4%Zn–0.25%Sn–0.1%Bi.

$$\text{anode efficiency } (\%) = \left(\frac{\text{theoretical weight loss corresponding to impressed current}}{\text{observed weight loss}} \right) \times 100$$

The experiment was repeated, at least twice, at each current density.

Results and discussion

Table 1 gives the corrosion rates of commercial aluminium, commercial Al–Zn binary alloy, commercial Al–Zn–Sn ternary alloys, and commercial Al–Zn–In–Bi quaternary alloys in alkaline citrate electrolyte solution. It can be seen that the addition of zinc enhances the corrosion rate. The solid-solubility of zinc in aluminium is about 5 wt.%. Hence, the addition of up to 5 wt.% zinc can be expected to give rise to perfect solid solutions of zinc in aluminium. Since zinc is cathodic to aluminium, its addition is expected to give rise to an alloy with a lower OCP. With the addition of 4 wt.% zinc to commercial aluminium, however, the resulting alloy shows an increase in OCP. This anomaly may be explained in terms of the formation of oxide-films on aluminium and Al–Zn alloy. It may be that Al–Zn alloy has less tendency to form an oxide film than has pure aluminium and, as a conse-

TABLE 1

Corrosion of quaternary alloys based on commercial aluminium (2S) containing zinc, indium, tin, and bismuth in alkaline citrate solution

Alloy composition (wt.%)	Weight loss (mg)	Corrosion rate ($mg\ cm^{-2}\ min^{-1}$)	Alloy ranking[a]
Al(2S)	193	0.322	
Al(2S)–4Zn	366	0.610	
Al(2S)–4Zn–0.025In	209	0.350	2
Al(2S)–4Zn–0.025In–0.01Bi	209	0.350	3
Al(2S)–4Zn–0.025In–0.05Bi	238	0.400	4
Al(2S)–4Zn–0.025In–0.1Bi	299	0.498	
Al(2S)–4Zn–0.025In–0.5Bi	252	0.420	7
Al(2S)–4Zn–0.025In–1Bi	319	0.532	
Al(2S)–4Zn–0.05In	167	0.2783	1
Al(2S)–4Zn–0.05In–0.01Bi	243	0.405	5
Al(2S)–4Zn–0.05In–0.05Bi	279	0.465	
Al(2S)–4Zn–0.05In–0.1Bi	247	0.4117	6
Al(2S)–4Zn–0.05In–0.5Bi	288	0.480	
Al(2S)–4Zn–0.05In–1Bi	391	0.553	
Al(2S)–4Zn–0.25Sn	402	0.670	
Al(2S)–4Zn–0.25Sn–0.01Bi	427	0.712	
Al(2S)–4Zn–0.25Sn–0.05Bi	495	0.825	
Al(2S)–4Zn–0.25Sn–0.1Bi	401	0.668	
Al(2S)–4Zn–0.25Sn–0.5Bi	693	1.155	
Al(2S)–4Zn–0.25Sn–1Bi	495	0.825	

[a]Best seven alloys in terms of corrosion resistance.

quence, this may result in faster corrosion of Al–Zn alloy. The corrosion rate is decreased markedly by the addition of indium to the Al–4% Zn-binary alloy. For the two ternary alloys, Al–4%Zn–0.025%In and Al–4%Zn–0.05%In, the latter gives the lower corrosion rate. Addition of bismuth to these ternary alloys does not cause any improvement in the corrosion rate. In fact, the corrosion rate is found to increase with increasing addition of bismuth in both systems. The best seven alloys, based on the corrosion rate, are specified in Table 1.

It is also seen from Table 1 that the addition of tin to the Al–4%Zn binary alloy increases the corrosion rate. Similarly, the addition of bismuth as the fourth element is also harmful.

Table 2 gives the steady-state OCP of different quaternary alloys of aluminium with zinc, indium, tin, and bismuth. Addition of tin to Al–4%Zn increases the OCP slightly: from −1.414 V to −1.419 V. It can now be considered that any of the ternary alloys Al–4%Zn–0.01 - 0.05%In may be suitable for further development. Further, the quaternary alloy of aluminium with 4%Zn–0.25%Sn–0.1%Bi exhibits a higher open-circuit potential (−1.460 V) than all the other alloys of this quaternary system (average potential −1.430 V). From these data, it is clear that the addition of indium proportionally increases the OCP of the Al–Zn binary alloy. Addition of bismuth as the fourth element only slightly enhances the OCP and there is no consistency between the change in OCP and the amount of bismuth

TABLE 2

Open-circuit potential (OCP) of commercial aluminium (2S) and its different quaternary alloys with zinc, indium, tin, and bismuth in alkaline citrate solution

Alloy composition (wt.%)	OCP (V)
Al(2S)	−1.340
Al(2S)–4Zn	−1.414
Al(2S)–4Zn–0.025In	−1.418
Al(2S)–4Zn–0.025In–0.01Bi	−1.428
Al(2S)–4Zn–0.025In–0.05Bi	−1.434
Al(2S)–4Zn–0.025In–0.1Bi	−1.451
Al(2S)–4Zn–0.025In–0.5Bi	−1.435
Al(2S)–4Zn–0.025In–1Bi	−1.446
Al(2S)–4Zn–0.05In	−1.436
Al(2S)–4Zn–0.05In–0.01Bi	−1.443
Al(2S)–4Zn–0.05In–0.05Bi	−1.442
Al(2S)–4Zn–0.05In–0.1Bi	−1.428
Al(2S)–4Zn–0.05In–0.5Bi	−1.440
Al(2S)–4Zn–0.05In–1Bi	−1.434
Al(2S)–4Zn–0.25Sn	−1.419
Al(2S)–4Zn–0.25Sn–0.01Bi	−1.420
Al(2S)–4Zn–0.25Sn–0.05Bi	−1.437
Al(2S)–4Zn–0.25Sn–0.1Bi	−1.460
Al(2S)–4Zn–0.25Sn–0.5Bi	−1.437
Al(2S)–4Zn–0.25Sn–1Bi	−1.433

added. This observation holds when bismuth is added as the fourth element, either to Al–4%Zn–0.025%In alloy or to Al–4%Zn–0.05%In alloy.

Table 3 shows the change in potential of different alloys of aluminium containing zinc, indium, tin, and bismuth in alkaline media, when they are anodically polarised at three different current densities, namely, 50, 100 and 150 mA cm^{-2}. It can be seen that the Al–4%Zn–0.025%In–0.1%Bi alloy is the best (*i.e.*, least polarising) alloy at each current density.

From Table 4 it will be seen that at 100 mA cm^{-2} and above, most of the alloys give very good anode efficiency values — of the order of 90% or above. Only a few alloys can be eliminated on the basis of low anode efficiency.

TABLE 3

Anodic polarisation of commercial aluminium (2S) and its different quaternary alloys with zinc, indium, tin, and bismuth in alkaline citrate solution

Alloy composition (wt.%)	Extent of anodic polarisation at:		
	50 mA cm^{-2}	100 mA cm^{-2}	150 mA cm^{-2}
Al(2S)	211	368	680
Al(2S)–4Zn	194	350	680
Al(2S)–4Zn–0.025In	256	458	544
Al(2S)–4Zn–0.025In–0.01Bi	130	466	694
Al(2S)–4Zn–0.025In–0.05Bi	246	410	724
Al(2S)–4Zn–0.025In–0.1Bi	93	192	278
Al(2S)–4Zn–0.025In–0.5Bi	131	228	333
Al(2S)–4Zn–0.025In–1Bi	122	305	457
Al(2S)–4Zn–0.05In	385	428	754
Al(2S)–4Zn–0.05In–0.01Bi	176	353	633
Al(2S)–4Zn–0.05In–0.05Bi	107	233	407
Al(2S)–4Zn–0.05In–0.1Bi	156	369	655
Al(2S)–4Zn–0.05In–0.5Bi	98	224	335
Al(2S)–4Zn–0.05In–1Bi	119	217	353
Al(2S)–4Zn–0.25Sn	102	289	402
Al(2S)–4Zn–0.25Sn–0.01Bi	99	296	427
Al(2S)–4Zn–0.25Sn–0.05Bi	111	324	495
Al(2S)–4Zn–0.25Sn–0.1Bi	124	343	401
Al(2S)–4Zn–0.25Sn–0.5Bi	128	348	693
Al(2S)–4Zn–0.25Sn–1Bi	125	257	495

Conclusions

(i) On the basis of weight-loss measurements, the best alloys are: Al–4%Zn–0.05%In, Al–4%Zn–0.025%In and Al–4%Zn–0.025%In–0.01%Bi.

(ii) The open-circuit potentials of the three alloys are −1.436 V, −1.418 V, and −1.428 V, respectively. These values are reasonably satisfactory.

TABLE 4

Anode efficiency of commercial aluminium (2S) and its quaternary alloys with zinc, indium, tin, and bismuth in alkaline citrate solution

Alloy composition (wt.%)	Anode efficiency (%) at: $mA\ cm^{-2}$					
	25	50	75	100	125	150
Al(2S)	28	61	75	90	91	96
Al(2S)–4Zn	50	72	89	96	98	96
Al(2S)–4Zn–0.025In	31	62	79	95	96	95
Al(2S)–4Zn–0.025In–0.01Bi	30	44	61	73	95	96
Al(2S)–4Zn–0.025In–0.05Bi	24	44	58	83	94	96
Al(2S)–4Zn–0.025In–0.1Bi	11	30	37	57	87	97
Al(2S)–4Zn–0.025In–0.5Bi	15	47	68	69	91	94
Al(2S)–4Zn–0.025In–1Bi	17	24	29	59	82	85
Al(2S)–4Zn–0.05In	38	52	79	91	96	96
Al(2S)–4Zn–0.05In–0.01Bi	39	52	76	94	95	95
Al(2S)–4Zn–0.05In–0.05Bi	12	17	51	65	91	97
Al(2S)–4Zn–0.05In–0.1Bi	15	40	61	83	94	99
Al(2S)–4Zn–0.05In–0.5Bi	19	38	41	71	84	88
Al(2S)–4Zn–0.05In–1Bi	29	50	70	79	92	93
Al(2S)–4Zn–0.25Sn	37	54	77	93	95	95
Al(2S)–4Zn–0.25Sn–0.01Bi	42	56	83	95	94	95
Al(2S)–4Zn–0.25Sn–0.05Bi	12	23	50	55	96	94
Al(2S)–4Zn–0.25Sn–0.1Bi	11	25	46	53	73	86
Al(2S)–4Zn–0.25Sn–0.5Bi	40	50	72	92	86	100
Al(2S)–4Zn–0.25Sn–1Bi	25	46	55	65	79	93

(iii) On the basis of anodic polarisation at 150 mA cm^{-2}, the least polarised quaternary alloy is Al–4%Zn–0.025%In–0.1%Bi.

(iv) The anode efficiency of almost all of the alloys is between 90% and 98% in the current density range 100 - 150 mA cm^{-2}.

(v) Taking into account the above four electrochemical properties, the quaternary alloy Al–4%Zn–0.025%In–0.1%Bi appears to be the best. Its characteristics are as follows:

Corrosion rate	0.498 mg cm^{-2} min^{-1}
OCP	−1.451 V
OCP at 150 mA cm^{-2}	−1.157 V
Anode efficiency at 150 mA cm^{-2}	97%

It is emphasized that this quaternary alloy is based on commercially available aluminium of only 99% purity. Hence, it is reasonable to assume that if the same alloy is prepared from more-pure aluminium much better electrochemical properties will be obtained.

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