

Summary

Certain reactor surfaces, such as metal oxides, are effective in promoting secondary reactions of propylene and ethylene at 700° C. Propane conversions also increase somewhat in such runs. The metal oxides on the reactor surfaces are at least partially reduced by hydrogen contact, and the oxides are also converted to a relatively durable, passive, metal sulfide layer by contact with sulfur-containing compounds.

The over-all order of reaction with respect to propane conversion is complex, and an assumed first-order gas-phase reaction yields rate constants which decrease significantly with increasing conversion.

Nomenclature

F	= molar flow rates, moles per unit time
k_c, k_c'	= rate constant, reciprocal time or unit volume per mole per time
P	= pressure, compatible units
R	= gas constant, compatible units
T	= temperature, compatible units
V_R	= reactor volume
x	= conversion of propane, moles reacted per mole of feed

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ALUMINUM AS A GALVANIC ANODE

Behavior in Sodium Hydroxide Solution Containing Calcium Hydroxide, Sodium Citrate, and Sodium Chloride

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To avoid waste of aluminum when used as a galvanic anode surrounded by caustic soda in a primary wet cell system, calcium hydroxide to saturation and sodium citrate at three concentrations were added to 1M sodium hydroxide solution containing 0.3% sodium chloride; this enhanced anode efficiency considerably. To understand the effects of the constituents, the anodic behavior of aluminum in the presence of these constituents was studied. The anode efficiency depends on the anodic current density and the presence of both calcium and citrate ions has a synergistic effect in promoting anode utilization. Efficiency of 60 to 98% can be attained in the current density range of 10 to 40 ma. per sq. cm.

FOR successful employment as a galvanic anode in a d.c. power source or for cathodic protection, aluminum should dissolve freely in the surrounding medium without film formation and should show a high negative potential. Though the possibility of using aluminum as a galvanic anode for cathodic protection has been mentioned (Applegate, 1960), Pryor and Keir (1957) have reported that there can be reversal of polarity when aluminum is coupled to graphite in chloride solution. To avoid this possibility it is desirable to make the environment around the aluminum alkaline, since higher negative potentials

can be achieved with aluminum in an alkaline than in an acidic medium and alkali can also complex with aluminum and keep it in solution.

However, Kapali and Subramanyan (1966b) found that aluminum employed as an anode coupled to graphite in sodium hydroxide solution is mostly wasted by self-corrosion, whereas substitution of sodium carbonate for sodium hydroxide (Kapali and Subramanyan, 1967) improved anode efficiency. But aluminum showed a tendency to become polarized in sodium carbonate and calcium hydroxide solutions. It was subse-

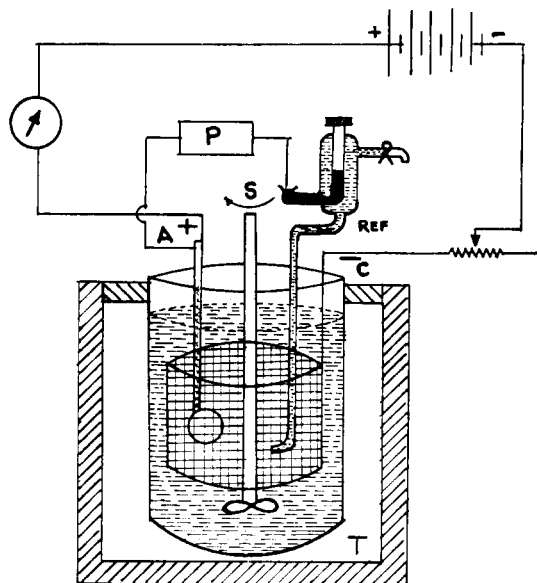


Figure 1. Circuit diagram for polarization of aluminum

- A. Anode
- C. Cathode gauze electrode (platinum)
- S. Stirrer
- P. Potentiometer
- Ref. Reference cell, Hg/HgO/1N NaOH
- T. Thermostat, $35^\circ \pm 0.1^\circ \text{C}$.

quently found that anode efficiency improved even in sodium hydroxide solution, if a soluble calcium compound was present (Kapali and Subramanyan, 1966a). These observations led to the development of alkaline solutions containing inhibitive and complexing agents suitable for the employment of aluminum as a galvanic anode (Kapali *et al.*, 1966a) and of Leclanché type primary wet cells (Kapali *et al.*, 1966c). Nearly two dozen primary wet cells based on such a solution have given satisfactory performance for more than two months. To understand the effects of the different constituents of the solution developed for primary wet cells, a systematic study of the anodic behavior of aluminum in the presence of the constituents was made.

Experimental

Solutions. The following solutions were prepared using laboratory reagent grade chemicals and distilled water:

- A. 1M NaOH + Ca(OH)₂ (0.1%) + NaCl (0.3%) + sodium citrate - Na₃C₆H₅O₇ · 2 H₂O (10%)
- A₁. 1M NaOH + Ca(OH)₂ (0.1%) + NaCl (0.3%) + sodium citrate (5%)
- A₂. 1M NaOH + Ca(OH)₂ (0.1%) + NaCl (0.3%) + sodium citrate (1%)
- A₃. 10% sodium citrate
- B. 1M NaOH + Ca(OH)₂ (0.1%) + NaCl (0.3%)
- C. 1M NaOH + Ca(OH)₂ (0.1%)
- D. 1M NaOH
- E. 1M NaOH + NaCl (0.3%) + sodium citrate (10%)

Electrodes. The anode was a circular specimen of aluminum (minimum 99% purity), each side of 1-sq. cm. area, with stem 12.5 cm. long.

The cathode was a tubular platinum gauze of an approximate area of 60 sq. cm.

The reference electrode was a Hg/HgO/1N NaOH half cell.

Procedure

The anode was polished with wet pumice powder, degreased with trichloroethylene, and weighed. It was then coated with paraffin wax so as to expose only one side of the specimen.

The experimental setup (Figure 1) consists of the anode surrounded by the cathode, placed in a 400-ml. borosilicate glass beaker containing 300 ml. of the electrolyte solution.

The anodic polarization was carried out by drawing current from a suitable combination of batteries and variable high resistances, keeping the solution stirred by means of a glass stirrer attached to a motor, and employing current densities from 2 to 80 ma. per sq. cm. All experiments were carried out at $35^\circ \pm 0.1^\circ \text{C}$. The duration of polarization was 1 hour for each current density and the steady potential of the anode was measured by means of an OSAW (Oriental Scientific Apparatus Workshop, Ambala Cantonment, India) slide-wire potentiometer with reference to the Hg/HgO/1N NaOH half cell.

At the end of the polarization, the anode was removed from the solution without switching off the current, washed thoroughly with distilled water, and dried in hot air. The specimen was weighed again after the wax coating had been removed with trichloroethylene.

From the weight loss of the specimen, the percentage utilization of anode was calculated according to the relation,

$$\text{Anode utilization (\%)} = \frac{\text{observed weight loss}}{\text{weight loss corresponding to impressed current}} \times 100$$

Results and Discussion

Reproducibility. The experiment at each current density was carried out at least five times and the average weight loss was taken for calculating the anode efficiency. The direct weight loss was also checked by volumetric estimation of aluminum in the solution (by titration with EDTA); good correlation between the two values was found. The reproducibility was, in general, of the order of 3% in all the solutions except sodium hydroxide alone, where the variation went up to 10%.

The anode potential was practically steady during the test period of 1 hour for a given current density. Between replicate experiments, it was reproducible within 30 mv.

Anode Utilization. The values of the anode utilization efficiency for aluminum in the various solutions at different current densities (Tables I and II) much exceed 100% in the lower range of current densities. This is to be attributed to local cell action and to negative difference or mechanical disintegration, sometimes referred to as "chunk" effect. From the current density at which the anode begins to become polarized, the values are below 100%. This may be caused by anodically formed oxide sticking to the specimen, since even with phosphoric acid-chromic acid treatment in these cases, the weight loss was less than the value calculated from the current passed. So it is concluded that at the lower current densities, wastage of aluminum is caused by local cell action and negative difference effect and at the higher current densities, passivation due to oxide-film formation obstructs free dissolution of the aluminum anode. Hence, for efficient utilization of aluminum as a galvanic anode, the current drain should be restricted to values at which waste and passivation are avoided.

Table I shows that for a given solution the anode utilization efficiency increases with current density (at lower current densities, values in excess of 100% indicate waste), reaches a maximum, and then decreases.

In analyzing the effects of the various constituents, the effect of the addition of sodium chloride to allow for the salt content of a typical saline soil can be seen in the lower anode utilization at current densities up to 30 ma. per sq. cm. in solution B than in solution C.

Considering solutions C and D, the effect of calcium in improving the efficiency is evident only beyond 10 ma. per sq. cm. However, if solutions B and E are compared, the anode utilization is in excess of 100% at all current densities up to 60

Table I. Effect of Solution Composition and Current Density on Anode Utilization of Aluminum

		$\left(\frac{\text{Observed weight loss}}{\text{wt. loss corresponding to impressed current}} \times 100 \right)$										
		% Anode Utilization of Aluminum at Various Current Densities, Ma. per Sq. Cm.										
No.	Electrolyte Composition	2	4	8	10	20	30	40	50	60	70	80
A	1M NaOH + Ca(OH) ₂ (0.1%) + NaCl (0.3%) + sodium citrate (10%)	1087 (9.2)	805 (12)	287 (35)	167 (60)	98	85	83	48	69	53	35
B	1M NaOH + Ca(OH) ₂ (0.1%) + NaCl (0.3%)	1282 (8)	730 (14)	321 (31)	346 (29)	181 (55)	122 (82)	109 (92)	92	82	79	78
C	1M NaOH + Ca(OH) ₂ (0.1%)	2041 (5)	805 (12)	625 (16)	417 (24)	157 (64)	107 (95)	107 (95)	102 (98)	85	77	86
D	1M NaOH	1818 (6)	833 (12)	350 (29)	333 (30)	201 (50)	132 (76)	110 (91)	134 (75)	90	84	76
E	1M NaOH + NaCl (0.3%) + sodium citrate (10%)	3125 (3)	1493 (7)	685 (15)	394 (25)	295 (34)	206 (49)	125 (71)	119 (84)	110 (91)	88	95

Values in parentheses are of anode efficiencies calculated according to the formula,

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

where anode utilization has exceeded 100.

Table II. Effect of Citrate Concentration on Anode Utilization of Aluminum in 1M Sodium Hydroxide Containing Calcium Hydroxide and Sodium Chloride

		Anode Utilization at Various Current Densities, Ma./Sq. Cm.			
No.	Electrolyte Composition	2	4	8	10
A	1M NaOH + Ca(OH) ₂ (0.1%) + NaCl (0.3%) + sodium citrate (10%)	1087 (9)	805 (12)	287 (35)	167 (60)
A ₁	1M NaOH + Ca(OH) ₂ (0.1%) + NaCl (0.3%) + sodium citrate (5%)	298 (34)	164 (61)	116 (87)	75
A ₂	1M NaOH + Ca(OH) ₂ (0.1%) + NaCl (0.3%) + sodium citrate (1%)	536 (19)	306 (33)	160 (63)	99

Table III. Anodic Polarization and Corrosion Behavior of Aluminum in Solutions Based on 1M Sodium Hydroxide

		Tafel Slope, Volt	Corrosion Potential, Volts vs. Hg/HgO/1N NaOH	Corrosion Current, Ma./Sq. Cm.		
				From Tafel plot	From observed corrosion rate	Observed Corrosion Mg./Sq. Cm./ Hr.
No.	Electrolyte Composition					
A	1M NaOH + Ca(OH) ₂ (0.1%) + NaCl (0.3%) + sodium citrate (10%)	0.68	-1.41	3.0	7.2	2.4
A ₁	1M NaOH + Ca(OH) ₂ (0.1%) + NaCl (0.3%) + sodium citrate (5%)	0.84	-1.42	2.8	6.6	2.2
A ₂	1M NaOH + Ca(OH) ₂ (0.1%) + NaCl (0.3%) + sodium citrate (1%)	0.36	-1.40	2.6	8.6	2.9
A ₃	Sodium citrate alone (10%)	0.15 ^a	-0.53	Negligible	Negligible	Negligible
B	1M NaOH + Ca(OH) ₂ (0.1%) + NaCl (0.3%)	0.50	-1.46	11.0	14.9	5.0
C	1M NaOH + Ca(OH) ₂ (0.1%)	0.26	-1.46	3.6	21.4	7.2
D	1M NaOH	0.05	-1.42	16.0	23.9	8.5
E	1M NaOH + NaCl (0.3%) + sodium citrate (10%)	0.11	-1.30	4.0	25.9	8.6

^a For 10% sodium citrate solution, slope is reported over one decade of current in microamperes.

ma. per sq. cm. in solution E indicating wastage. Considering solutions A, B, and E, the wasteful corrosion of the aluminum anode up to the current density of 20 ma. per sq. cm. is lower in solution A than in either B or E, with only one exception (solution B at 4 ma. per sq. cm.). This clearly brings out the synergistic effect of the calcium-citrate combination in solution A.

With the idea of economizing in the use of citrate, two concentrations lower than 10% were tried and the anode utilization efficiencies found in the current density range 2 to 10 ma. per sq. cm., so as to correspond to the values normally met with in Leclanché type primary wet cells (Table II). It is seen that 5% of citrate in the solution is more effective in reducing self-corrosion than 10 or 1%.

Polarization. Figures 2 and 3 bring out the anodic polarization behavior of aluminum in the various solutions. Highly negative potentials for aluminum are obtained in 1M sodium hydroxide solution containing citrate, whereas in solution A₃

containing citrate alone, the potentials are much less negative (Figure 2) and aluminum is appreciably polarized even at 100 μ a. per sq. cm.

Curves A to E show that the anodic polarization is less steep in solutions D and E than in the others, and least steep in E. This behavior is indicative of greater dissolution of aluminum in solution E than even in sodium hydroxide alone, brought about by the complexing action of citrate on aluminum, and is corroborated by the increased values of anode utilization in this solution (Table I), compared to the other solutions. However, citrate in combination with calcium decreases the wasteful consumption of aluminum. This is also borne out by the fact that the anodic polarization curve is steeper in solution A than in either B or E. The values of the slopes of the portion (indicated by arrows in Figures 2 and 3) of the polarization curves taken to represent the Tafel region are given in Table III, along with the corrosion potentials of aluminum in the various solutions and the values of corrosion currents (i_{corr}) as estimated

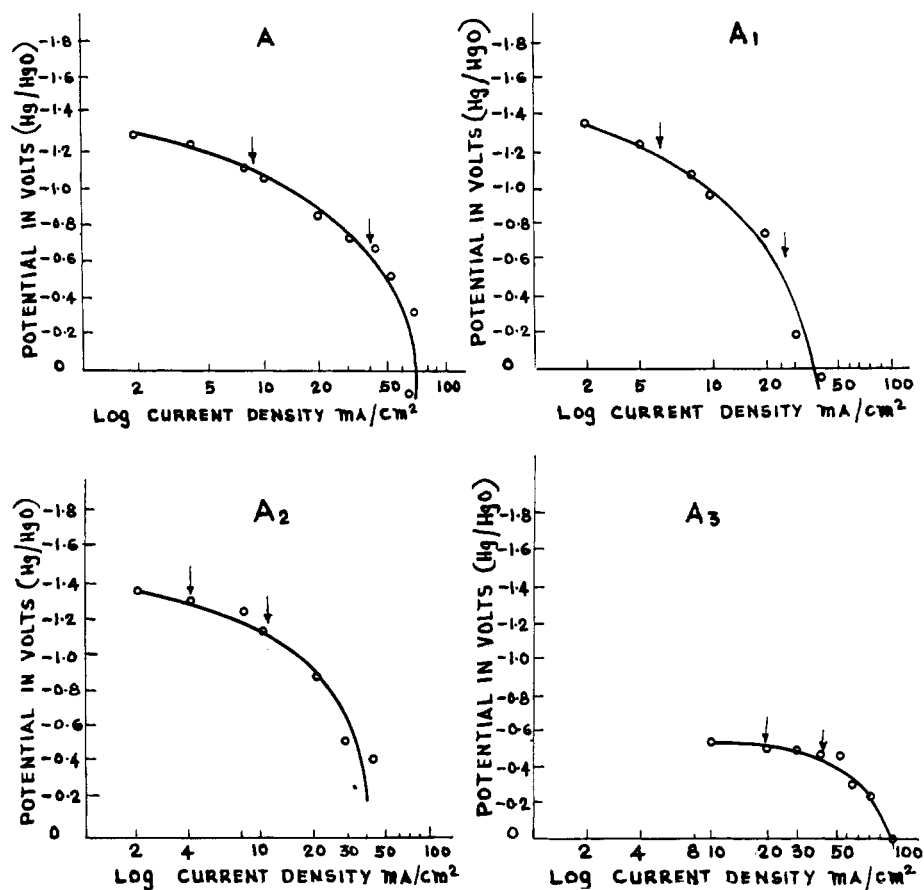


Figure 2. Influence of citrate on anodic polarization of aluminum (2S) in solutions based on sodium hydroxide (A, A₁, and A₂) and in neutral citrate alone (A₃)

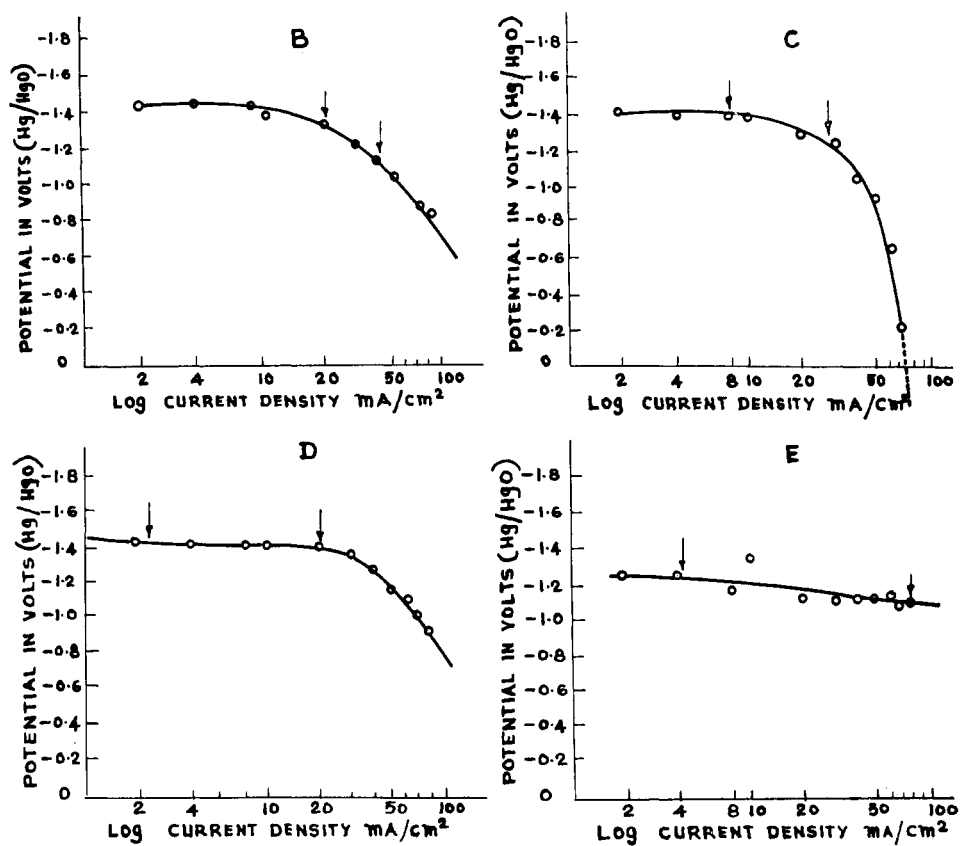


Figure 3. Anodic polarization of aluminum (2S) in solutions based on sodium hydroxide

from the Tafel plot and calculated from actual weight-loss data. The slopes were measured at a region before that indicating concentration polarization.

The special effect of 5% citrate in combination with calcium as in solution A₁ is substantiated by the maximum value of the slope obtained with this solution.

It is believed that the synergistic action of calcium and citrate in reducing the self-corrosion of aluminum employed as anode in sodium hydroxide solution may be due to a complex compound of calcium and citrate. The following mechanism is suggested to explain the effect. At 1% citrate concentration, the complex formed, though inhibitive, might be adsorbed as discrete entities with the calcium ions disposed towards the metal surface so that aluminum could still be attacked at the exposed portions. With the increase in concentration of the citrate to 5%, the discrete complexes may tend to get attached to form bigger ligands, enhancing the coverage of the metal surface by these clusters. The possibility of the formation of metal chelates in solutions of high alkalinity containing additional hydroxo ligands has been reported (Chaberek and Martell, 1959). With further addition of citrate, there is, perhaps, excess citrate left over after the formation of clusters with calcium to enhance the corrosion rate by complexing with aluminum, since in the absence of calcium, citrate in the sodium hydroxide solution accelerates the corrosion of aluminum (solution E).

Among the solutions free of citrate, solution B containing sodium chloride gives a higher slope than the other two. The corrosion current calculated from natural corrosion is also less in solution B. This is contrary to the report (Putilova *et al.*, 1960) that chloride ions accelerate the corrosion of aluminum in alkalis; however, the idea of specific adsorption of halogen ions (Iofa *et al.*, 1964) may, perhaps, be invoked to explain the inhibitive effect of the chloride ions.

The values of corrosion current from observed natural corrosion and from polarization data do not agree. This discrepancy is to be attributed to the fact that the system studied is a complicated one, representing a polyelectrode on which several reactions like self-corrosion, anodic dissolution, and passivation may be taking place. Further, the surface also is continuously changing and the different ions in the solution have different effects on the electrode behavior.

Conclusions

The waste of aluminum used as a galvanic anode in 1M sodium hydroxide solution can be considerably reduced by addition of calcium hydroxide and sodium citrate to the solution and by choosing suitable current density. It is known (Cessna *et al.*, 1964) that calcium can have corrosion-inhibitive action in addition to chromate when employed as calcium chromate and that metallic cations can reduce the corrosion of metals in acidic solutions (Buck and Leidheiser, 1958). Calcium and citrate are synergistic in improving the anode utilization of aluminum in 1M sodium hydroxide solution and anode utilization of the order of 60 to 98% can be attained in the current range of 10 to 40 ma. per sq. cm. in solution containing 10% citrate and 34 to 37% in the range of 2 to 8 ma. per sq. cm. in solution containing 5% citrate.

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