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Electrolysis of Sodium Silicate Solutions Using Cation-Exchange Membranes

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Abstract

The electrolysis of sodium silicate solutions was studied at various temperatures, current densities, and concentrations. By using a cation-exchange membrane, NaOH was recovered at high current efficiency in the cathodic compartment. Sodium silicate solutions in the anodic compartment were upgraded to products of higher SiO_2/Na_2O ratios. The deposition of silica on anodes strongly inhibits smooth operation during electrolysis, and a semibatch method is described to overcome this difficulty.

Sodium silicate solutions are commercially produced by melting a mixture of quartz sand and sodium carbonate in glass furnaces. The solidified masses are then dissolved in autoclaves to give aqueous products. Commercial products usually do not have fixed chemical compositions. The ratio of its two components (SiO_2/Na_2O) varies typically from 1 to 4 according to the amounts of silica and soda ash charged to the furnace. The main disadvantage of this process is its high energy cost in the fusion step. An alternate process for eliminating the fusion step is to dissolve quartz sand directly into caustic soda solution. While the alternate process does save a considerable amount of energy, its products are limited to high-alkaline sodium silicates with a silica to sodium oxide ratio less than about 2.6. For many industrial applications of sodium silicates such as in silica-gel manufacture, the use of high-alkaline sodium silicate is undesirable since it not only represents a waste of Na_2O but also because of the acid required for neutralization.

Various methods have been proposed to raise the SiO_2/Na_2O ratio of sodium silicate solutions including dissolution of amorphous silica, ion exchange, dialysis, and electrolysis (*1*). None of them, so far, has attained

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commercial value unless under special circumstances. The method of electrolysis to remove Na_2O from sodium silicate solutions were attempted by many early workers such as Treadwell and Wieland (*2*), Collins (*3*), and Praetorius and Wolf (*4*) long before ion-exchange membranes became available, and recently by Iler (*5*), Lieb and Sugano (*6*), and Schenker et al. (*7*). In these recent studies, detailed methods for the preparation of stable concentrated silica sols were worked out using cation-exchange membranes in electrolysis. There has been very little study, however, for the purpose of upgrading high-alkaline sodium silicate solutions to the products of higher SiO_2/Na_2O ratios which are commonly produced by the fusion process.

PRINCIPLE OF THE PROCESS (Fig. 1)

A single cell consisting of two compartments separated by a piece of cation-exchange membrane is shown in Fig. 1. During the electrolysis, sodium cations pass through the membrane and are discharged at the cathode to form NaOH and hydrogen. The anodic reaction involves the discharge of hydroxide ion to form oxygen and water. The overall reaction is therefore the decomposition of water into hydrogen and oxygen with a net effect of transfering NaOH from the anodic to the cathodic compartment. The sodium silicate solution originally present in the anodic compartment is upgraded to a more desirable solution (with less Na_2O content) for certain applications. Dilute NaOH solution initially charged to the cathodic compartment is

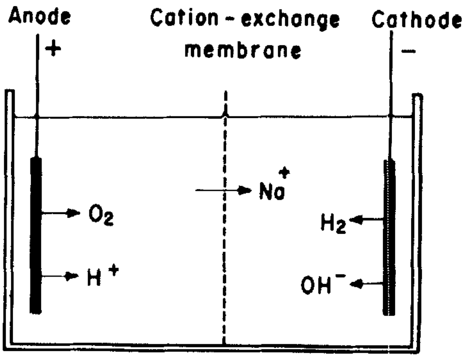

FIG. 1. Single cell and principle of electrolysis.

enriched with more NaOH to a stronger solution which can be recycled back to the autoclave for silica digestion.

EXPERIMENTAL

A rectangular cell (7.5 cm long, 10 cm wide, 5 cm high) made of acrylic plastic was used in the experiments. A piece of cation-exchange membrane fitted with neoprene gaskets separated the cell into two compartments. The electrodes used were made of stainless steel 304 plates of 40 cm^2 geometric area. Electrode separation was 3.5 cm and the cell temperature was maintained within ±0.2°C via an adjustable electric heater immersed in the anolyte.

Batch Experiments

Both compartments were initially charged with a high-alkaline sodium silicate solution. After the solutions had reached the desired temperature, electrolysis was started. During the run, electric current was maintained constant via a galvanostat, and cell potential was monitored with a strip-chart recorder. When a sharp rise of cell potential was observed, the circuit was interrupted and both catholyte and anolyte were analyzed for their SiO_2 and Na_2O contents. Variables used in the experiments were temperature (20, 50, 70°C), current density (10, 30, 100 mA/cm^2), and sodium silicate concentration (17, 29, and 41 Baumé).

Semibatch Experiments (Fig. 2)

The semibatch operation permits the cell to treat a much larger amount of solution. In the operation, sodium silicate and sodium hydroxide solutions were circulated separately by two pumps between cell compartments and their corresponding reservoirs. The operating temperature was 60°C and the variables were current densities (5, 12.5, 37.5 mA/cm^2) and sodium silicate concentration (15, 25, 36 Bé). Starting with a sodium silicate solution with a SiO_2/Na_2O ratio of ~2.3 in the anodic compartment and reservoir, and with a dilute NaOH solution (~3%) in the cathodic compartment and reservoir, the electrolysis proceeded until the cell potential rose sharply. The electrolytes were then analyzed and the current efficiencies were calculated according to Faraday's law.

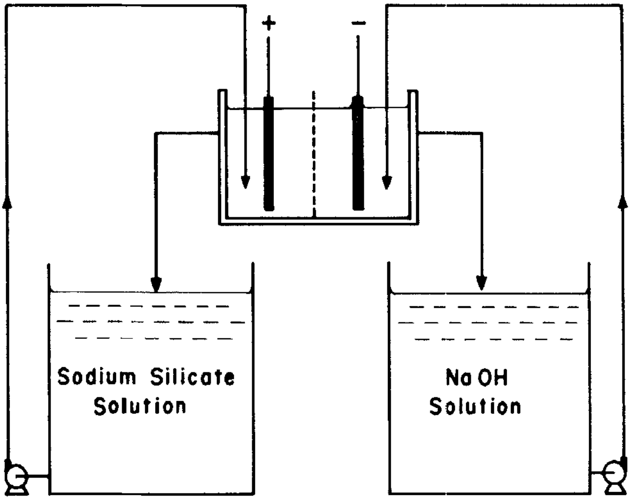

FIG. 2. Semibatch arrangements.

RESULTS AND DISCUSSIONS

During batch experiments, electrolysis usually proceeded smoothly until the cell potential started to rise sharply which was caused by the deposition of silica on the anode. If the circuit was not interrupted, the anode would soon be coated with a thick layer of silica which almost insulates the electrode. The deposits were removed by hot caustic solution and the anode was polished with sandpaper to brightness before being used again. A typical electrolysis curve is shown in Fig. 3 in which the cell potential remains relatively stable until silica starts to deposit at about 80 min. Figures 4 and 5 show the relationship between cell potential and current density at various temperatures and concentrations, respectively. As expected, higher temperatures and concentrations result in a lower cell potential at the same current density. For all batch runs, current efficiencies were good, ranging between 88 and 97%. The time when silica deposition starts after the initiation of electrolysis is strongly dependent on current density and solution concentration. As shown in Figs. 6 and 7, low current and concentration tend to prolong electrolysis time without silica deposition. The deposition was thought to be caused by the combined effects of adsorption of silicate ions on the positive electrode and gelation of silica sol near the electrode at a relatively low pH value.

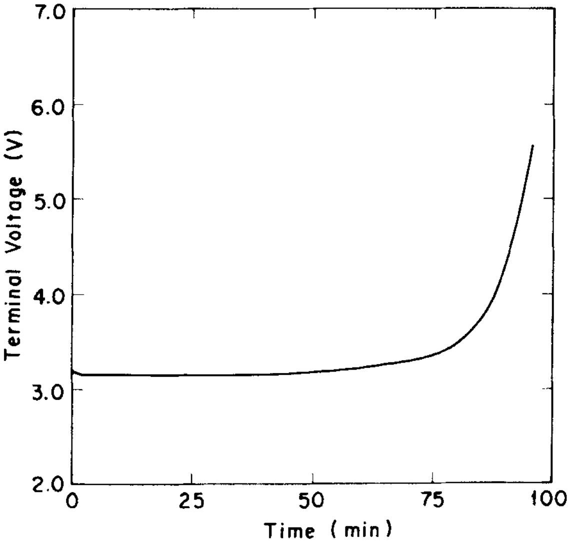

FIG. 3. Change of terminal potential in a typical run.

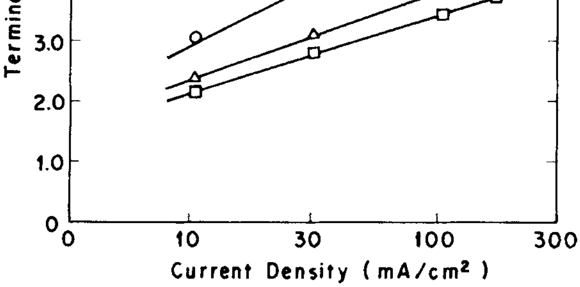

FIG. 4. Terminal voltage–current density relationship at various temperatures.

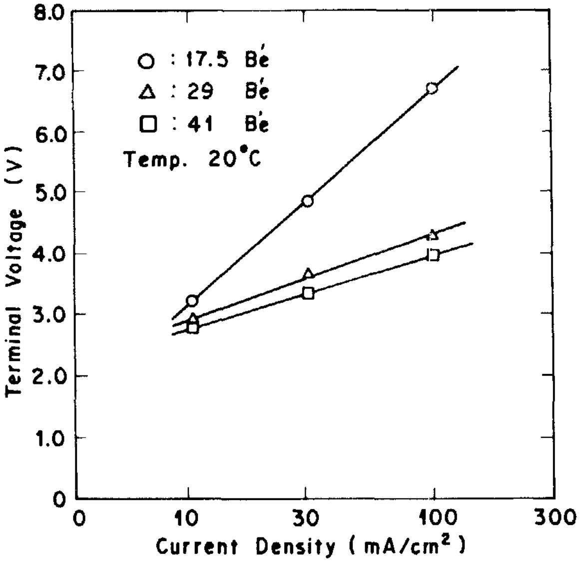

FIG. 5. Terminal voltage–current density relationship at various sodium silicate concentrations.

The semibatch results indicate that the final SiO_2/Na_2O ratio in the solution depends largely on the solution concentration. Current density in the range of study had no significant effect on the final SiO_2/Na_2O ratio. Cell potential, of course, increases with increasing current as in the batch experiments. With reservoirs holding about 500 mL of solution, electrolysis times were about 5 times longer than those in batch cell. Figure 8 shows the relationship between the final SiO_2/Na_2O ratio and the starting solution concentrations.

When a run was started with an already-coated anode and a fresh silicate solution ($SiO_2/Na_2O \approx 2.3$), the cell potential was initially high but decreased to its stable value over a short period of time, typically 10 to 20 min. This indicates that the already deposited silica was dissolved back into the solution. An overly coated electrode, however, did not dissolve back. It is therefore important to interrupt the circuit in time so that the lightly coated anode could be restored in the fresh silicate solution without a cleaning effort. For this reason, semibatch operations at specified conditions were run repeatedly to test whether anodes could be used repeatedly. During the test, a controller was used to interrupt the circuit when the cell potential exceeded about 3 V over its stable value. The electrolytes were then replaced with fresh solutions and electrolysis was resumed until the controller interrupted

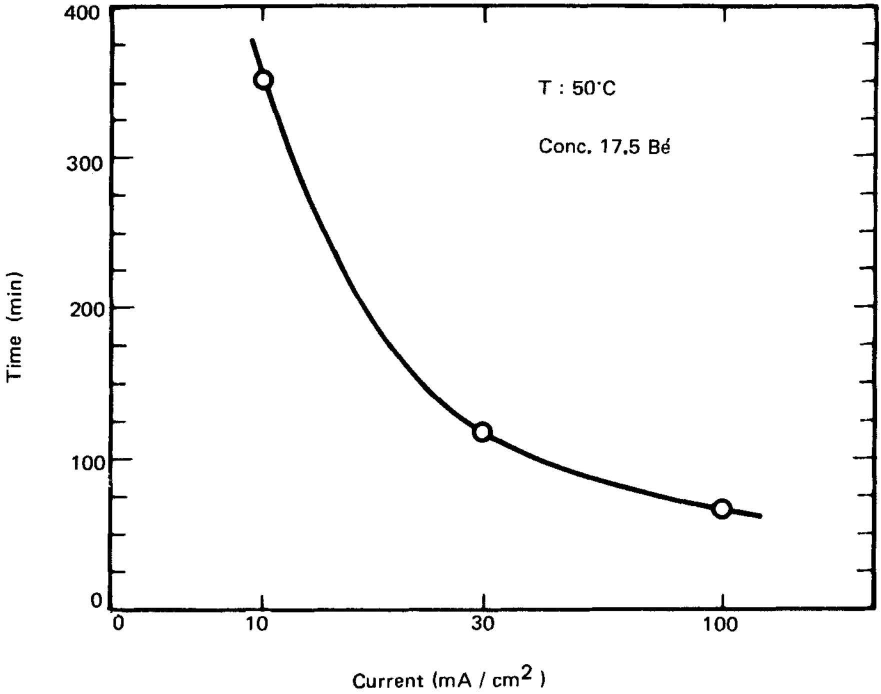

FIG. 6. Duration of electrolysis before silica deposition at various current densities.

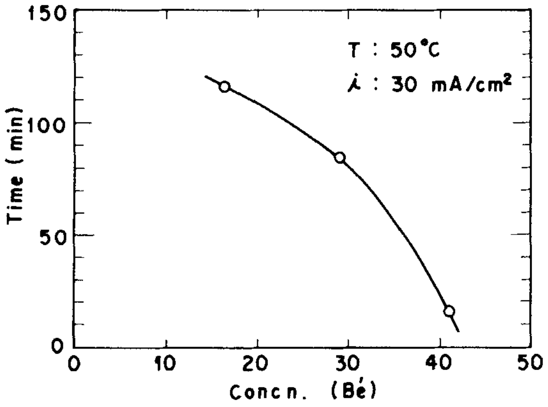

FIG. 7. Duration of electrolysis before silica deposition at various sodium silicate concentrations.

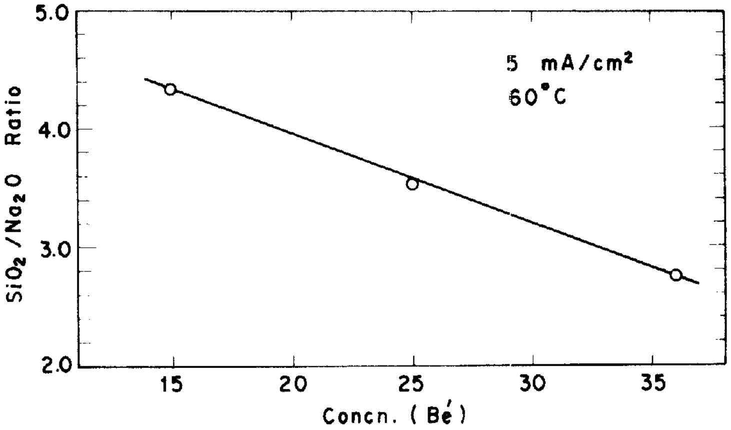

FIG. 8. Final SiO_2/Na_2O ratio at various initial sodium silicate solutions.

the circuit again. Table 1 shows the results of one set of semibatch experiments with six repeated runs at 12.5 mA/cm^2, and 60°C, and 25 Bé starting concentration. Both cell potentials and current efficiencies remained stable (2.8 V and ~87%) over six successive runs, indicating that anodes can be used repeatedly without any noticeable side effect. Products from each run had an SiO_2/Na_2O ratio about 3.2, which is suitable for many applications such as silica-gel production. NaOH was recovered as a ~5% solution, which is suitable for caustic dilution in the autoclave digestion.

TABLE 1
Successive Runs at 12.5 mA/cm^2 and 25 Bé

Run no.	1	2	3	4	5	6
Duration (h)	15.38	22.58	18.42	16.00	29.62	35.33
Cumulative hours	15.38	37.96	56.38	72.38	102.0	137.33
Weight of fresh solution (g)	500	588	500	443	966	1000
Cell voltage (V)	2.80	2.80	2.80	2.80	2.80	2.80
SiO_2/Na_2O ratio:						
Initial	2.34	2.34	2.30	2.30	2.31	2.30
Final	3.18	3.42	3.20	3.30	3.10	3.29
Current efficiency:						
Cathodic (%)	87.46	87.00	84.61	87.98	81.87	88.80
Anodic (%)	87.80	89.22	84.70	88.09	85.54	90.06
Time average current efficiency		cathodic = 86.20%		anodic = 87.74%		

CONCLUSION

Sodium hydroxide can be recovered and sodium silicate solutions upgraded simultaneously by electrolysis with cation-exchange membranes at high current efficiencies. Results show that the final SiO_2/Na_2O ratio of the upgraded silicate solution depends largely on the initial concentration. A higher SiO_2/Na_2O ratio requires a lower concentration to start with. The most troublesome phenomenon during electrolysis was the deposition of silica on the anodes. To overcome this difficulty, semibatch operations in which silica-deposited anodes were repeatedly restored by fresh silicate solutions without a cleaning effort were demonstrated. Overdeposition on anodes, however, should be avoided.

REFERENCES

1. J. G. Vail, *Soluble Silicates,* Reinhold, New York, 1952.
2. W. D. Treadwell and W. Wieland, *Helv. Chim. Acta, 13,* 842 (1930).
3. T. Collins, U.S. Patent 1,562,940 (1925).
4. M. Praetorius and K. Wolf, German Patent 482,177 (1925).
5. R. K. Iler, U.S. Patent 3,668,088 (1972).
6. D. F. Lieb and T. T. Sugano, U.S. Patent 4,124,471 (1978).
7. B. A. Schenker et al., U.S. Patent 4,203,822 (1980).

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