A METHOD FOR CONTINUOUS MONOSILANE GENERATION
UTILIZING MOLTEN SALT ELECTROLYSIS

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ABSTRACT

We investigated and developed a practical and continuous production of monosilane via parallel reactions in a single molten salt bath consisting of electrolysis of LiCl, hydrogenation of Li and a chemical reaction of LiH and SiCl₄. In the normal electrolysis, a bypass current is generated due to Li attached at the anode chamber and at the diaphragm. This bypass current caused production problems and efficiency degradation. We were able to substantially minimize this current by moving the attached Li away from these surfaces electrolytically and by blowing chlorine aimed at the displaced Li during electrolysis. When the electrolysis was performed at 1000 A, this method yielded current efficiencies of electrolysis and eventual monosilane generation of 97.5% and 92%, respectively.

INTRODUCTION

Photovoltaic electric power generation has been receiving attention as a source of clean energy which could replace oil. Among silicon photocells, amorphous silicon cells, as compared to single crystal silicon cells, use far less material and are better suited for mass production. For this reason, Japan's Sunshine Project placed a great emphasis on development of amorphous silicon photocells. As a part of the effort, this project was conducted to develop a monosilane production method; monosilane being the raw material for amorphous silicon films. Continuous monosilane production employing molten salt electrolysis was proposed by W. Sundermeyer some 25 years ago (1,2), and L.M. Ritz, et. al. attempted development for commercialization which was not successful(3,4).

When the oil shock hit the world in 1974, we re-examined the process because of its low energy and low natural resource consumption. Our basic research started in 1975. The process we employed is given
in Figure 1. Each of three reactions requiring a molten salt bath takes place in a sealed molten salt vessel. The main feature of the present investigation is that the reactions take place continuously and in parallel (5). As compared to the work carried out by past investigators, the present process and apparatus possess many advantageous features such as: safety when equipment is broken or fails functionally, ability to handle pressure variations, reliable material transport, and ease of start-up and or maintaining operation. This project was supported by the Sunshine Project since 1980 as a commercialization research effort.

This commercialization research was carried out with the closed cycle apparatus, consisting of a monosilane generation apparatus shown in Figure 2, plus a silicon chlorinator, a silicon tetrachloride separation and recovery unit, and a monosilane purifier. The initial design had a problem with a valve operation in transporting the molten salt. This problem was solved by employing an overflow transport method and a simple pump with no moving parts actuated by gas pressure. This modification made it possible to reliably run the hydrogenation and monosilane generation reaction, and it clearly exposed the electrolysis problems.

When the electrolysis is performed at 2000 to 3000 A, the current efficiencies of electrolysis and of monosilane generation were 90 and 80%, respectively. These are essentially satisfactory numbers for production of metals by molten salt electrolysis in general. However, there were signs which gave doubts about long-term operability, such as erosion of the anode, a sudden drop of the anode chamber pressure, accumulation of Li on the salt bath surface, etc.

We discovered that, as shown in Figure 3(Left), a bypass current is generated through the anode chamber caused by Li in the Li collector and by Li attached on the diaphragm. In the case of the anode chamber which is separated and electrically isolated from the rest, another bypass current is generated caused by Li attached on the anode chamber as shown in Figure 3(Right). And the bypass current causes electrolysis between the anode chamber and the anode, depositing Li on the inside surface of the anode chamber wall. Thus, if the bypass current is eliminated, we believe that the various problems preventing commercialization will be solved and that the current efficiencies would approach the theoretical values.

THE EXPERIMENT

In order to eliminate the bypass current in the apparatus shown in Figure 2, the following steps were attempted:
(a) By raising the voltage potential of the anode chamber and the diaphragm with respect to the cathode and by means of dissolution and deposition of the attached Li, the Li can be transferred to the cathode and to other surfaces.

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(b) Some Li, which moves to places other than the cathode by the above process, may float on the molten salt and may reattach itself to the anode chamber. In order to prevent this phenomenon from happening, the Li is eliminated by injecting chlorine and forming LiCl.

In order to carry out the above corrective measures, the following revisions to the apparatus were made:

(a) The anode chamber equipped with the diaphragm was separated from the collector and electrically isolated from the rest.

(b) A "Li transport power source" was installed between the anode chamber equipped with the diaphragm and the cathode.

(c) A chlorine blow-in tube was installed below the molten salt surface at a place between the anode chamber and the closest equipment to it, which are the outer jackets covering three cathode leader rods. This location is expected to be the main Li transfer point.

(d) A chlorine recovery chamber was added which is electrically isolated and which surrounds the anode chamber and the cathode leader rod outer jackets. This addition is a safety measure to prevent the outside of the reaction chambers from filling with reactive chlorine.

Figure 4 shows the cross-sectional view of the monosilane generation test set-up after the modifications.

The following steps are used to run the test apparatus. First, introduce the raw material, salt, into the molten salt vessel. Cover the vessel with a simple lid, dry the material, melt and dehydrate. Next, replace the lid with the one from which all equipment is hung, and then start the electrolysis. As Li begins to appear at the cathode, it will float as droplets, be collected in the collector, and be transferred via a transfer tube to the hydrogenator. The hydrogenator is filled with hydrogen, and the hydrogen is added as it is consumed to maintain the hydrogenator pressure. Moreover, the molten salt is fed at a constant rate from the molten salt vessel by a overflow mechanism. Li, which enters the hydrogenator, is hydrogenized to form LiH, is immediately dissolved in the molten salt and is fed to the silane generation chamber. Since an excess amount of SiCl₄ is continually fed into the chamber, the LiH which flows in will react to produce SiCl₄ and LiCl. The latter will flow out to the molten salt vessel dissolved in the salt. Thus, the Li cycle is completed and it is possible to operate the electrolysis continuously for a long period of time.

The following test parameters were employed:

The electrolysis current was automatically controlled at 1100 A.

The maximum voltage potential at the anode chamber was set at

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2.6 V above the cathode potential. This voltage was applied at the start of the electrolysis. This potential takes into account the 0.5 V margin against the apparatus corrosion, and the figure was computed in the following way. Also, when the Li transport current exceeded its maximum value of 100 A, the voltage was adjusted to keep the current at around 100 A.

\[ V_{\text{max}} = \{V_t - I_x(R_a + R_c) - E_0\} \times \left(\frac{R_1}{R_2}\right) + (E_0 - E_1) - V_p \]

Where,
- \( V_t \): Applied electrolysis voltage
- \( R_a, R_c \): Anode and cathode resistance
- \( I_x \): Electrolytic current
- \( E_0 \): Decomposition Voltage of LiCl at 400°C
- \( E_1 \): Electrolytic potential of Ni/NiCl<sub>2</sub> against C/Cl<sub>2</sub> at 400°C
- \( R_1 \): Molten salt resistance between the cathode and the diaphragm
- \( R_2 \): Molten salt resistance between the anode and the cathode
- \( V_p \): Voltage margin for corrosion prevention. (Voltage drop due to the anode chamber and the cathode leader rods, etc.)

From the start of the electrolysis, chlorine was blown in through three nozzles at the rate of 0.5 l/min. Chlorine was diluted with twice the volume of argon. This volume is about one tenth of chlorine generated at the anode during electrolysis.

Main dimensions in the electrolysis area are: the anode: 30cm OD by 60cm long; the cathode: 42cm ID by 60cm long (crown shaped); the diaphragm: 35cm ID by 65cm long (10 mesh screen made of Ni). The salt bath temperature was maintained at 400°C in the molten salt vessel and at 570°C in the hydrogenator.

Since it is difficult to directly measure the bypass current, the effect was compared by computing the electrolysis efficiency and the monosilane production efficiency and also by observing the test apparatus during and after the operation. The efficiencies were computed by the following definitions.

- The current efficiency of electrolysis = \( \frac{\text{Li(mol) calculated from } H_2 \text{ consumed}}{\text{Theoretical Li(mol) Value based on the electrolysis current}} \)

- The current efficiency of monosilane production = \( \frac{\text{SiH}_4 \text{(mol) actually collected}}{\text{Theoretical SiH}_4 \text{(mol) production based on the electrolysis current}} \)

RESULTS AND DISCUSSION

Test operations were made at a constant electrolysis current of 1100 A. The Li transport power source was turned on and chlorine was
injected to minimize the bypass current. Test results are given in Table 1. Observation of the electrolysis section was made after test runs with the Li transport power source (total electrical consumption was $1.1 \times 10^3$ coul.). There was no corrosion on the anode surface near the salt level which normally is the most susceptible to corrosion. Even tool marks were still visible. The diaphragm and the anode chamber were also quite healthy.

For a comparison, tests were conducted without the Li transport power source and without chlorine injection. Results are given in Table 2. These test results have not changed much from those obtained in the past with a similar set-up. On the other hand, table 1 shows that there were no phenomena observed which preclude commercialization and that the electrolysis efficiency increased substantially and approached that of the theoretical values. Thus, we believe that these improvements are due to minimization of the bypass current and are not due to hardware or its arrangement.

The same conclusion can be reached by observing the voltages (the cathode as the base) vs. elapsed time at key equipment. When the bypass current is present, a large drop in electrolysis voltage is observed (Fig.6) in the early stage of the electrolysis when the electrolysis current is kept constant. On the other hand, when the bypass current is eliminated by the use of the Li transport power source and the chlorine injection, the electrolysis voltage stays constant throughout as shown in Fig.5. Also, when the bypass current was present, the voltage at the anode chamber decreased and the Li collector increased. Since these voltage values approach the short circuit values when the electrical pass is from the anode chamber to the Li collector via the salt bath surface, the main bypass current is thought to be flowing from Anode - Anode Chamber - Li Collector - Cathode (the bypass current II) rather than from Anode - Anode Chamber - Diaphragm - Cathode (the bypass current I).

The reason for the above is that the bypass current I is constant because it is only created by attaching around the diaphragm of a portion of Li freed from the cathode during electrolysis. On the other hand, the bypass current II is created mainly by Li attached on the exterior surface of the anode chamber. In other words, during electrolysis between the anode and anode chamber due to the bypass current I, Li is freed which is transferred out to the molten salt bath. The Li then floats on the surface of the bath and is attached to the anode chamber. The bypass current II does not flow until this happens. This floating Li causes an undesirable process cycle. Namely, it will create the bypass current II and the Li moves to attach itself to the nearest equipment. Since the floating Li is replenished continually, the attached Li will refloat and reattach to the anode chamber creating more bypass current II. This cycle is repeated. The bypass current deposits Li on the inside surface of the anode chamber, which subsequently increases the floating Li, and which further increases the bypass current II. This vicious cycle continues and the
bypass current increases until the limit is reached which is determined by the resistance of the molten salt and the voltage of electrolysis. The result is that during a long-term operation, a large amount of Li is accumulated on the molten salt surface.

Figure 7 and 8 show the relationship between the current consumption for Li transport during operation and the relative voltage potential of the anode chamber (diaphragm) or of the Li collector. The anode chamber voltage and the resistance to Li transport vary depending on the location and amount of Li attached. However, in comparison with the early stage of operation, the current drops and the voltage stabilizes toward the end of the run. The early fluctuation may be due to the floating Li left over from the earlier run.

Table 3 shows the current and power consumed for transporting Li. This indicates that about 2% of the total Li was attracted to the anode chamber in the normal operation. The maximum current used to transport Li in the test was 100 A. So, the objective was accomplished below one-tenth of the electrolysis current. When a Ni-made apparatus shown in Figure 4 is used to perform electrolysis at 5000 A, the electrolysis voltage will be 8.5 V, and the maximum voltage and current required to transport Li would be about 5.5 V and 500 A, respectively.

CONCLUSION

Tests were conducted to commercialize a new monosilane production method which utilizes electrolysis of a molten salt. The main objective of the investigation were to remove undesirable phenomena during electrolysis and to improve the efficiency by eliminating the cause of the problems, i.e., by minimizing the bypass current flowing through the anode chamber.

It was possible to sufficiently remove the bypass current by the following method: raise the voltage potential of the anode chamber and the diaphragm with respect to the cathode, transport Li from the diaphragm to the cathode, and attract Li at the anode chamber to the nearest equipment and then blow in chlorine to remove Li as LiCl. A further finding is that the anode chamber can be protected from corrosion by selecting the proper voltage potential.

The overall effect of the elimination of the bypass current was that the current efficiency of electrolysis increased from 90% to 97.5%. Also, it became possible to make a long-duration run while maintaining high efficiency. Moreover, we found that there is no danger of floating Li after shutdown and that it is easy to maintain the equipment.
### REFERENCES

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### TABLE 1. Test Run Data with Li Transport Power Source and Chlorine Injection.

| Electrolytic Current (A avg.) | 1104 | Quantity of Electricity ($10^6$ Coul.) | 23.8 | Hydrogen Consumed (mol.) | 120.4 | Monosilane Produced (mol.) | 56.6 | Current Efficiency of Electrolysis(%) | 97.5 | Monosilane Production(%) | 91.8 |
|-------------------------------|------|----------------------------------------|------|--------------------------|------|---------------------------|------|--------------------------------------|------|--------------------------|------|
| Li Accumulation on the Bath    | NO   | Sudden Pressure Drop in the Anode Chamber | NO |                          |      |                           |      |                                      |      |                          |      |

### TABLE 2. Test Run Data without Li Transport Power Source and Chlorine Injection, before and after Modifications. (Conventional Electrolysis)

| Apparatus Used | Apparatus Used |
|----------------|----------------|
| Fig.2          | Fig.4          |

| Electrolytic Current (A avg.) | 2104 | Quantity of Electricity ($10^6$ Coul.) | 468.5 | Hydrogen Consumed (mol.) | 2230 | Monosilane Produced (mol.) | 1027 | Current Efficiency of Electrolysis(%) | 91.8 | Monosilane Production(%) | 83.8 |
|-------------------------------|------|----------------------------------------|-------|--------------------------|------|---------------------------|------|--------------------------------------|------|--------------------------|------|
| Li Accumulation on the Bath    | YES  | Sudden Pressure Drop in the Anode Chamber | YES |                          |      |                           |      |                                      |      |                          |      |
| (Conventional Electrolysis)    |      |                                         |      |                          |      |                           |      |                                      |      |                          |      |

### TABLE 3. Electric Current and Power Consumption in Transporting Li.

| Mode        | Mean Current (A) | Current Ratio (%) | Power Ratio (%) |
|-------------|------------------|------------------|-----------------|
| Electrolysis| 1104             | 100              | 100             |
| Li          | 1st half         | 53.1             | 4.0             | 2.3             |
|             | 2nd half         | 25.1             | 2.3             | 1.1             |
| Transport   | Mean             | 41.4             | 3.7             | 1.8             |

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SiH₄ Generation Apparatus

Figure 1. Principle of our Monosilane Generation Method.
1. Molten Salt Vessel
2. Heater
3. Anode
4. Cathode
5. Diaphragm
6. Anode Chamber
7. Outer Jacket
8. Li Collector
9. Transport tube
10. Hydrogenator
11. Salt Pump
12. Monosilane Generation Chamber
13. Salt Bath Lid
14. Electrolysis Power Source

Figure 2. The Original Monosilane Production Apparatus Design Used in This Investigation. (Cross-sectional View)

Figure 3. Main Passages of Bypass Current and Mechanisms of Current Generation. (1 = LiCl electrolysis, 2 = Movement of Li by dissolving and Depositing, 3 = Current Path through Metal, 4 = Li - Cause of Bypass Current Generation.)
Figure 4. Revised Monosilane Production Apparatus to Prevent Bypass Current (Cross-Sectional View).

Figure 5. Voltages of each parts during the Test Run to prevent the Bypass Current.

Voltage of the electrolysis (Vt), Anode chamber voltage (Vw) and Collector voltage (Vco) are given with respect to the Cathode.
Figure 7. Relationship between the Current for Li Transport and the Li Collector Voltage above the Cathode.

The current readings are the maximum and the minimum over time. The proportional relationship is maintained only at the stable minimum current for a short duration as the current drop. It appears that the main Li transport comes from Li attached around the diaphragm.

Figure 8. Relationship between the Current for Li Transport and the Anode Chamber Voltage above the Cathode.

The current readings are the maximum and the minimum over time. Since the proportional I-V relationship is maintained, it is believed that the large current is due to the movement of Li attached around the anode chamber. The main current is believed to be flowing in the bypass current II path.