Electrolytic Separation of Lithium Isotopes in Aqueous Solutions of Lithium Hydroxide Using a Mercury Cathode

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The separation factor, α, for lithium isotopes in the electrolysis of aqueous solutions of lithium hydroxide at a streaming mercury cathode has been investigated as a function of temperature, current density and electrolyte concentration. At 25°C a separation factor of 1.069 ± 0.004 was obtained in 5 M LiOH at a current density of 0.25 A/cm². The separation factor and the difference in activation energy of the isotopes for the electrolytic process were found to be dependent of the studied parameters.

In a previous paper,[1] a detailed description is given of experiments on isotope separations of lithium in aqueous lithium chloride solutions with a mercury cathode, as well as a summary of similar investigations previously made.[2-9] Only two of the references deal with lithium hydroxide solutions.[4,9] Taylor and Urey[4] obtained a separation factor, α, of 1.020, at 25°C with a constant current density of 0.62 A/cm². Perret, Rozand and Saito[9] found $\alpha = 1.043$ at 30°C with a current density decreasing from 0.2 to 0.02 A/cm.² In both of the experiments the electrolyte concentration gradually decreased during the electrolysis. In the present investigation, a systematic study has been made of the effects of current density, concentration of electrolyte and temperature on the separation factor.

The Rayleigh distillation formula has been used [4,9] in calculating the true separation factor, α. However, by using a large volume of electrolyte and short time of electrolysis, the change in isotopic composition of the electrolyte is negligible and the simpler expression $\alpha = R'/R$ can be applied, where R' is the ratio of the mole fraction of lithium-6 to the mole fraction of lithium-7 in the amalgam formed at the mercury cathode during the electrolysis, and R is the corresponding ratio in the electrolyte. Additionally, the separation factor is obtained at constant electrolyte concentration.

The over-all reaction in the process is

$$2 \text{ LiOH(aq)} \rightarrow 2 \text{ Li(Hg)} + \tfrac{1}{2} \text{ O}_2 + \text{H}_2\text{O}$$
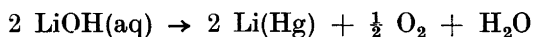
By using streaming mercury, a continuously renewed cathode surface is maintained during the electrolysis.

The formation of an amalgam instead of the evolution of hydrogen at the cathode is due to the high hydrogen overvoltage on mercury, especially at high current density according to the Tafel relationship. The various steps involved in the isotope separation will be discussed below.

EXPERIMENTAL

Apparatus. The apparatus, Fig. 1, was the same as that previously employed.[1] A few electrolyses (marked I) were, however, made with the conical base exchanged for a polyethylene plate with a small inward slope to the drainage tube (see inset, Fig. 1). This makes it possible to use a much smaller protective layer of carbon tetrachloride (1.3 cm instead of 8 cm). The effects of this layer are discussed below.
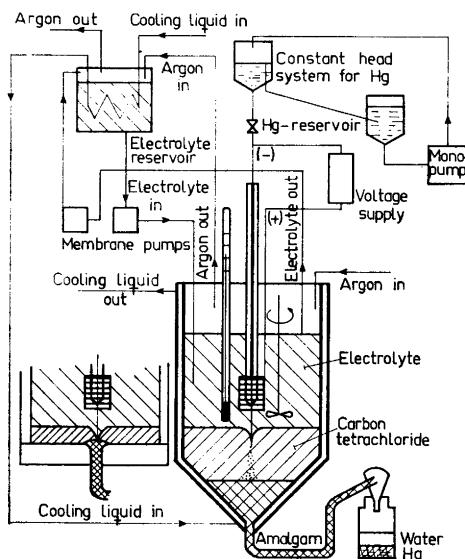

Fig. 1. The electrolysis apparatus.

Chemicals. The mercury was treated in the same manner as before.[1] The electrolyte was made up from lithium hydroxide (Merck, min. 98 %, impurity lithium carbonate) and demineralized water. The carbonate concentration of the lithium hydroxide solution was checked by titration with standard acid. It was found to be less than 1 %. During the electrolysis the solution was flushed with a large amount of argon in order to carry away evolved oxygen and keep out the carbon dioxide.

Electrolysis. The electrolyses were performed with constant speed of circulation (10 litres/h) of the electrolyte (2—5 litres) and with a constant mercury stream (4 kg/h).

The current was kept constant during each run while only small fluctuations occurred in the resulting voltage. The temperature was held within $\pm 1-2°C$. The stirring rate was also kept constant. In the amalgam the concentration of lithium varied from about 0.0003 % by weight at low current densities to about 0.02 % at the highest values. The cathode area was about 0.2 cm².

For a more detailed description see Ref.[1] In comparison with the lithium chloride experiments, the lithium hydroxide system gave slightly fewer gas bubbles and electrolyte droplets in the carbon tetrachloride section of the cell.

Chemical analysis. The current efficiency was determined by titration of the lithium hydroxide solutions obtained from the reaction of the amalgam with water, with standard dilute nitric acid, and comparing this figure with values calculated according to Faraday's law. The titrated solution was then evaporated in teflon cups and the dry lithium nitrate kept in closed polyethylene tubes for mass analysis.

Mass analysis. The mass analyses have been carried out at the Dept. of Physics at Chalmers University of Technology, Gothenburg. For details concerning the mass analyses and their error see Ref.[1]

The standard deviation, about 0.25 % of R and R', gives the standard deviation in α, $\sigma_\alpha = 0.004$ (Ref.[1]). Results from comparable experiments confirm the calculated error.

RESULTS AND DISCUSSION

Current efficiency. The current efficiency is defined as the ratio of the number of gram atoms of lithium in the amalgam to the number of faradays used in the electrolysis. Figs. 2 and 3 show how the current efficiency varies with temperature, current density, and concentration of the electrolyte.
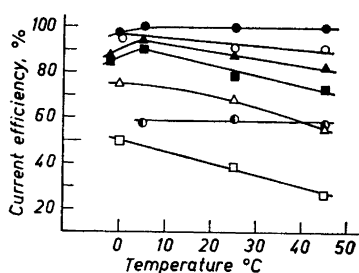

Fig. 2. Current efficiency as a function of temperature. 5 M LiOH: ● 5 A/cm²; ▲ 1 A/cm²; ■ 0.5 A/cm². 1 M LiOH: ○ 5 A/cm²; △ 1 A/cm²; □ 0.25 A/cm². 0.1 M LiOH: ◑ 0.5 A/cm² (see Apparatus).
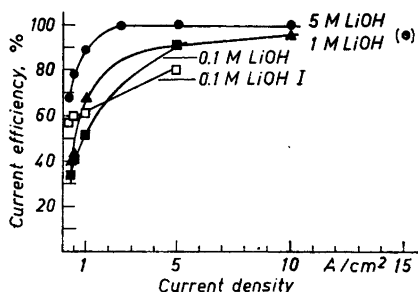
Fig. 3. Current efficiency as a function of current density at 25°C. For series 0.1 M LiOH I see Apparatus.

One possible explanation of the deviation from 100 % is that absorbed solution starts a back reaction

$$\text{Li(Hg)} + \text{H}_2\text{O} \rightleftharpoons \text{Li}^+ + \text{OH}^- + \tfrac{1}{2}\,\text{H}_2$$

when the amalgam drops are separated from the mercury cathode and are falling through the carbon tetrachloride section of the cell.

To avoid a possible back reaction, one series of electrolyses was carried out using a thinner protective layer of carbon tetrachloride (1.3 cm instead of 8 cm). This meant that the mercury stream held together just down to the amalgam pool in the bottom of the cell and was not split up into drops. With this cell design the current efficiency for 0.1 M LiOH becomes much higher at low current densities (see Fig. 3, curve 0.1 M LiOH I). At high current density, however, the efficiency is less than in the corresponding experiment with more protective liquid. Part of the explanation is probable that a film

of solution follows the amalgam to the pool, where back reaction occurs. In the case of a thick carbon tetrachloride layer this film may be washed off before the drops reach the pool.

The formation of hydrogen instead of lithium metal at the cathode

$$H_2O + e^- \rightarrow \tfrac{1}{2} H_2 + OH^-$$
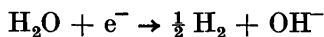
is also possible, especially at low current density, where the overpotential of hydrogen is lower. Impurities in the mercury and in the electrolyte also affect the hydrogen over-potential.[10] The low current efficiency in 0.1 M LiOH may also be due to the relatively higher concentration of H_3O^+ which favours the relase of primary hydrogen.

From Fig. 4, where the relative values of the amounts of lithium lost per unit time (*i.e.* $(1-C) \cdot I$ where C is the current efficiency and I is the current) in the different electrolyses are given, it is apparent that the losses of lithium in the electrolyses at different current densities, electrolyte concentrations and varying the cell-design show a complicated pattern. In spite of the high concentration of lithium metal at the cathode at high current density the release of primary hydrogen is low.

The scope of the present investigation does not, however, permit any more detailed interpretation of the side or back reactions.

To what extent the current efficiency affects the separation factor has not been evaluated, but no significant difference of α in two series of electrolyses in 0.1 M LiOH has been found, one using the ordinary cell and the other with reduced protection layer (LiOH I).

Dependence of the separation factor, α, on current density at various electrolyte concentrations. Fig. 5 shows the variation of α at different current densities and concentrations at 25°C for lithium hydroxide, with lithium chloride curves from Ref.[1] superimposed. In comparison with the lithium chloride system a more distinct increase of α is shown at decreasing current density
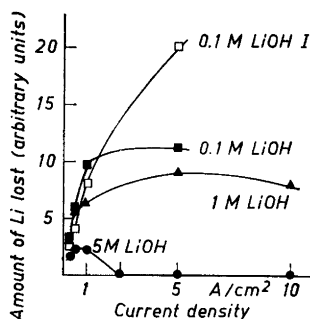

Fig. 4. Amount of lithium lost per unit time as a function of current density at 25°C. For series 0.1 M LiOH I see Apparatus.
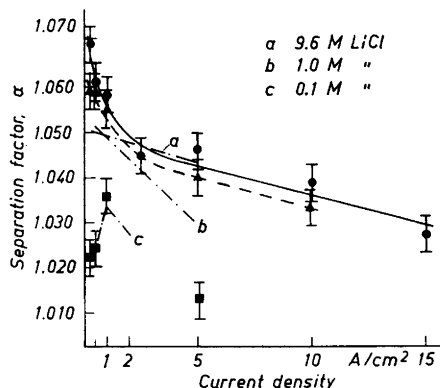
Fig. 5. Separation factor, α, as a function of current density at 25°C. ● 5 M LiOH; ▲ 1 M LiOH; ■ 0.1 M LiOH.

in 5 and 1 M LiOH. The effect on α of the change of the concentration from 5 M to 1 M LiOH is small. In 0.1 M LiOH, however, the α values are considerably lower as previously observed with 0.1 M LiCl [1] and show a similar pattern.

As discussed in Ref.[1] the difference in hydration ability of the lithium at various concentrations can not explain the variations of α.

The current density effect on α is presumably partly due to the increase of the temperature at the cathode when higher currents are used and the ohmic drop in the Helmholtz double layer which increases with the depletion
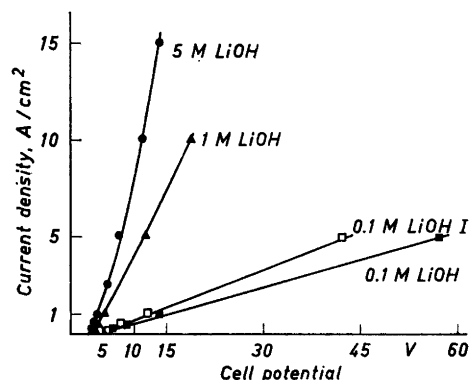

Fig. 6. Current density as a function of cell potential at 25°C. For series 0.1 M LiOH I see Apparatus.

of lithium ions, see below. The increased concentration of lithium metal on the cathode surface at high current density may also diminish the differences between the reaction rates of the two isotopes. Fig. 6 shows the cell potentials at the current densities used.

The electrochemical behaviour of lithium hydroxide and lithium chloride does not differ widely. Lithium hyroxide is, however, not fully dissociated in aqueous solutions. The equilibrium

$$LiOH \rightleftharpoons Li^+ + OH^-$$

has a dissociation constant of $K = 0.7$ (Ref.[11]). * Therefore this dissociation can affect the isotope separation process at the cathode. The rate-determining step of the separation can, in such a case, involve the dissociation of the lithium species. The low α's in 0.1 M LiOH are difficult to explain, but as the current efficiency is low, released hydrogen at the cathode surface gives different conditions for the electrolytic process. Even the back reaction may have an effect, but as the α values did not change when the current efficiency is raised, (series LiOH I), other reactions must play an important part at low electrolyte concentration. However, present knowledge of the electrode reactions is not sufficient for a more sophisticated discussion. Work on electrode processes mostly deals with very dilute solutions of the reactants and with a high concentration of supporting electrolyte as in polarography. The current densities

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* *Added in proof.* Later determination published in *Acta Chem. Scand.* **18** (1964) 521 by H. Ohtaki, gives $K = 1.5$.
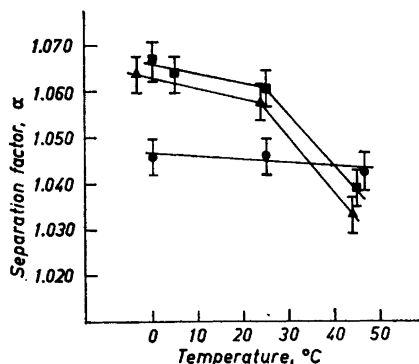
Fig. 7. Separation factor, α, as a function of temperature in 5 M LiOH. ■ 0.5 A/cm²; ▲ 1 A/cm²; ● 5 A/cm².
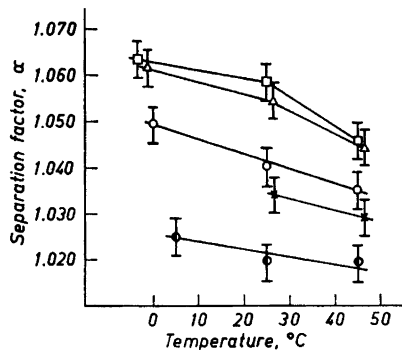
Fig. 8. Separation factor, α, as a function of temperature in 1 M and 0.1 M LiOH. 1 M LiOH: □ 0.25 A/cm²; △ 1 A/cm²; ○ 5 A/cm²; × 10 A/cm². 0.1 M LiOH I: ◐ 0.5 A/cm² (see Apparatus).

used are also often low, less than 10^{-2} A/cm² and applied for very short times.[12,13] It must also be added that the influence of impurities in the mercury and electrolyte could be important, but that in the present investigation the influence is thought to be constant and does not interfere in the comparison of the effects of the parameters.

Temperature dependence. Electrolyses were carried out at temperatures between −3° and +45°C for serveral current densities and electrolyte concentrations, Figs. 7 and 8. From the curves one can suppose that at least two different reactions are involved in the separation process. Again, however, the actual conditions at the electrode are not sufficiently well known to allow further treatment of the results. The true temperatures in the region of the cathode area may deviate somewhat from the stated ones. Between 5 M and
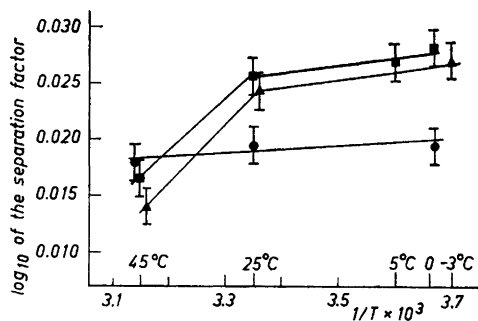

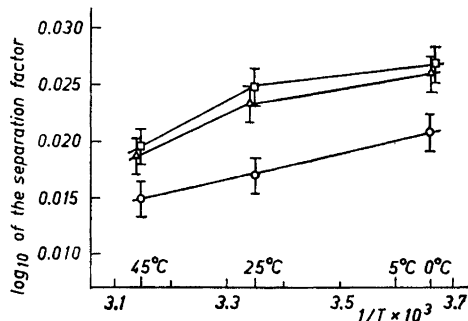Fig. 9. Log₁₀ of the separation factor as a function of temperature in 5 M LiOH. ■ 0.5 A/cm²; ▲ 1 A/cm²; ● 5 A/cm².

Fig. 10. Log₁₀ of the separation factor as a function of temperature in 1 M LiOH. □ 0.25 A/cm²; △ 1 A/cm²; ○ 5 A/cm².
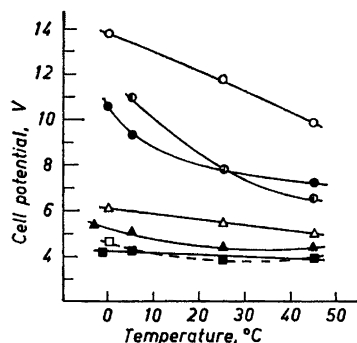
Fig. 11. Cell potential as a function of temperature. 5 M LiOH: ● 5 A/cm²; ▲ 1 A/cm²; ■ 0.5 A/cm². 1 M LiOH: O 5 A/cm²; △ 1 A/cm²; □ 0.25 A/cm². 0.1 M LiOH I: ◐ 0.5 A/cm² (see Apparatus)

1 M LiOH the difference in temperature dependence of the separation factors is small in the temperature interval from 0° to 25°C. Between 25° and 45°C this difference is greater at the highest concentration at low current density. At high current density the temperature dependence diminishes, probably because of the great amount of heat developed in the depleted cathode region and which nullifies temperature changes in the bulk of the solution. This phenomenon can also explain the small variation, if any, of α in 0.1 M LiOH between 5° and 45°C, Fig. 8.

From Figs. 9 and 10 the difference in activation energy $\Delta E_a = E_6 - E_7$, where E_6 and E_7 are the activation energies of the over-all separation process for ^6Li and ^7Li, respectively, can be calculated according to the Arrhenius equation

$$\frac{d \ln\alpha}{d(1/T)} = - \frac{\Delta E_a}{R}$$

Assuming ΔE_a to be constant between 25° and 45°C and between 0° and 25°C, ΔE_a becomes about -220 cal/mole at high, and -35 cal/mole at low temperatures in 5 M LiOH. In 1 M LiOH the corresponding values are -110 cal/mole and -35 cal/mole.
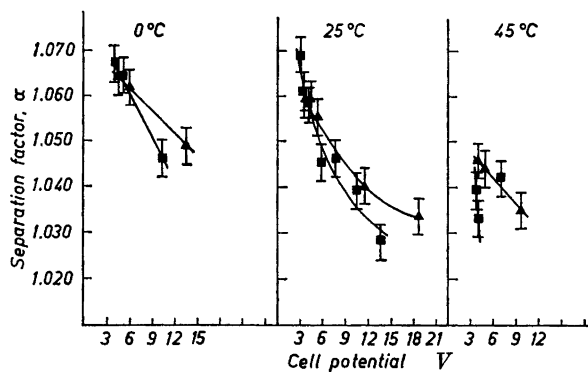

Fig. 12. Separation factor, α, as a function of cell potential at different temperatures.
■ 5 M LiOH; ▲ 1 M LiOH.

In the discussion above, the current density is used as a parameter. If however, α is plotted against potential instead of current density, Fig. 12, no different picture emerges, because of the small deviation from linearity between current density and cell potential, Fig. 6 and 11.

CONCLUSIONS

It is shown that the electrolytical separation process at a mercury cathode for lithium isotopes is sensitive to changes of electrolyte concentration, current density or potential, temperature and the anion of the lithium salt. The separation factor is significantly higher in hydroxide solution than in chloride solution at low current density and high electrolyte concentration. The reason for this difference may be the stability of the LiOH molecule in aqueous solution.

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