

## Isotope Effects in Electrolysis of Solid Lithium Hydride

BENGT COLLÉN

Research Institute of National Defence, FOA 4,  
Stockholm 80, Sweden

The isotope effect in countercurrent electromigration in molten lithium salts has been extensively studied (for references see Ref.<sup>1</sup>). The salt-like and somewhat peculiar character of the hydride<sup>2</sup> suggested that it would be interesting to investigate if the empirical relation given by Klemm,<sup>3</sup> for the isotope effect in the electrolyses of molten halides could be applied. The present study was started initially on the electrolysis of molten lithium hydride, but as no non-conductive material which could resist the corrosion of the molten hydride was found, the interest turned to solid lithium hydride. On solid salts, however, only a few studies of the isotope effects in electrolysis have been made,<sup>3-9</sup> of the lithium compounds only lithium sulfate has been studied.<sup>7-9</sup>

Lithium hydride is a good conductor of electricity,<sup>2</sup> the specific conductivity is  $3.7 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$  at 600°C and shows no discontinuity at the melting point of 688°C. The electrode reactions are, at the cathode  $\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$  and at the anode  $\text{H}^- \rightarrow 1/2 \text{H}_2 + \text{e}^-$ .

High purity lithium hydride powder from Foote Mineral Company, USA, was pressed in an argon atmosphere into cylindrical rods, 1 cm in diameter and about 5 cm in length, with a density of 94 % of theoretical.

The electrolytic cell<sup>10</sup> is shown in Fig. 1. The anode surface is a net made of stainless steel and a pool of molten zinc in the bottom of the cell serves as the cathode.

The hydride rod was fitted with two supporting spiral rings and placed in the supporting tube. The cell was previously degassed and flushed with argon and hydrogen. The cell was slowly heated to about 570°C in a hydrogen atmosphere. The electrolysis current was measured with a copper coulometer. At the beginning of the electrolysis the resistivity was high but decreased rapidly presumably due to increased metallic conduction. Generally after a few hours fluctuations of the current frequently increased and short circuiting

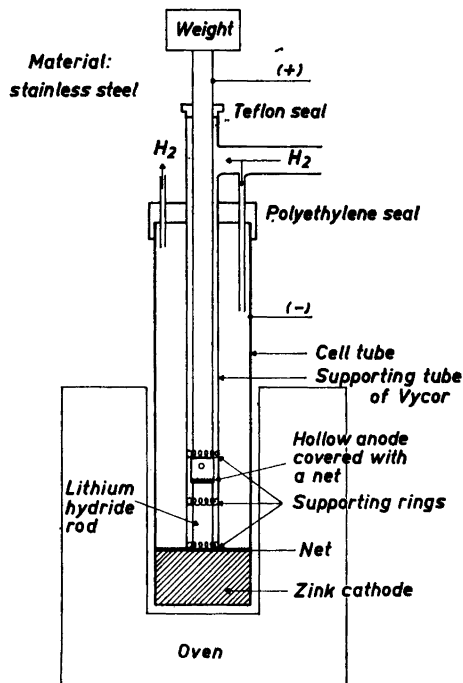


Fig. 1. The electrolytic cell.

occurred and therefore the electrolysis had to be discontinued.

After cooling the lithium hydride rod was taken out and examined. At the anodic end usually some reaction with traces of oxygen and water in the cell-atmosphere had occurred; otherwise the hydride was in an unchanged condition. The resulting rod was cut into small plates, the lengths of which were measured. The plates were then converted to lithium nitrate solutions for analysis.

The lithium content in the samples was determined by weighing as lithium sulfate. The isotopic composition was measured in a mass spectrometer at the Dept. of Physics at Chalmers University of Technology, Gothenburg; see Ref.<sup>8</sup>

It was found that the length of the hydride rod decreases in agreement with calculations according to Faraday's law. The decrease in length occurs only at the anodic end. This indicates that the transport number of lithium in lithium hydride is close to 1 at about 600°C. The scavenger cathode of zinc showed no reaction with the hydride.

From the quantity of electricity used, the isotopic composition and the total amount of lithium along the anodic end of the rod both before and after the electrolysis, the mass effect,  $\mu^+$ , for lithium as the hydride can be calculated according to Klemm.<sup>11</sup> An enrichment of lithium-7 was always found at the anodic end. The experimental difficulties mentioned above allowed the passage of only a small quantity of electricity, resulting in a small total enrichment. Therefore only the very approximate minimum value,  $\mu^+ = -0.04$ , could be obtained. This value is, however, in agreement with Klemm's empirical relationship for the halides.<sup>3</sup> A small enrichment of lithium-7 at the cathodic end of the hydride rod was also found.

*Acknowledgement.* The author wishes to thank Dr. A. Lundén for valuable discussions. The English of this paper has been corrected by Dr. R. Whiteker.

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Received April 13, 1964.

## Algal Carotenoids

### III. The Oxygen Functions of Fucoxanthin

ARNE JENSEN

*Norwegian Institute of Seaweed Research, N.T.H., Trondheim, Norway*

**F**ucoxanthin, the characteristic carotenoid of brown algae and of diatoms, has been given the chemical composition  $C_{40}H_{54-60}O_6$ .<sup>1-5</sup> Except for one sample

of fucoxanthin which analysed as  $C_{40}H_{54}O_6$  in the hands of Willstätter,<sup>1</sup> the analytical data given in the literature agree fairly well and indicate a content of six oxygen per forty carbon atoms for this pigment. Heilbron and Phipers<sup>4</sup> suggested that two of the oxygen atoms were present in carbonyl groups while four formed secondary hydroxyl functions. Retrovsky<sup>6</sup> has proposed a hexaol structure for fucoxanthin. On the basis of infra-red absorption data Liaaen and Sørensen<sup>7</sup> and Torto and Weedon<sup>5</sup> proposed the presence of one conjugated keto group and one isolated carbonyl function (or unsaturated ester<sup>5</sup>) in fucoxanthin. In two previous communications<sup>8,9</sup> we have shown that fucoxanthin contains one secondary (or primary) hydroxyl group, and we obtained evidence for the presence of at least two tertiary hydroxyl functions in the molecule. The presence of one carbonyl group in conjugation with the polyene chain was proven, and the presence of an absorption band at  $1732\text{ cm}^{-1}$  (isolated carbonyl function) in the infra-red spectrum of the pigment was verified.

We now want to present evidence to show that the isolated carbonyl absorption band at  $1732\text{ cm}^{-1}$  in the infra-red spectrum of fucoxanthin is associated with an acetoxy group. The infrared spectrum of fucoxanthin monoacetate<sup>8</sup> already indicated that fucoxanthin contained an acetoxy group, as the acetylation led to an increase in the intensity of the  $1732$  and  $1240\text{ cm}^{-1}$  bands without introducing any new bands. In addition, perhydrofucoxanthin obtained in our laboratory by catalytic hydrogenation (Adams catalyst) of fucoxanthin in ethyl acetate as well as in acetic acid showed absorption peaks at  $1735$ ,  $1245$  (acetate) and  $1720\text{ cm}^{-1}$  (isolated carbonyl). The first two peaks disappeared upon saponification.

The nuclear magnetic resonance spectrum of fucoxanthin in deuteriochloroform was kindly recorded by Dr. A. Melera on a Varian A-100 spectrometer and showed the presence of eleven methyl groups in the molecule; one more than the ten methyls of a normal carotenoid. One sharp peak with a  $\tau$ -value of 7.97 clearly indicated the presence of a methyl group in an acetoxy function.<sup>10</sup> This was confirmed by quantitative determination of acetyl groups according to the method of Pregl-Roth<sup>11</sup> which gave 0.8 mole of acetic acid per mole of fucoxanthin (calc. as  $C_{44}H_{62}O_6$ ; average of four determinations). The volatile acid