Electrical Resistivity of Liquid and Solid Lithium

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The electrical resistivity of lithium contained in a stainless steel capillary has been determined from 15 to 460 °C by means of a Kelvin–Wheatstone bridge. The resistivity of the liquid between 180 and 460° obeys equation (i)

$$\rho_l/\Omega\ \mathrm{m} = 16{\cdot}476 \times 10^{-8} + 4{\cdot}303 \times 10^{-10}\theta_c - 2{\cdot}297 \times 10^{-13}\theta_c^2 \qquad \text{(i)}$$

where θ_c is in °C. The corresponding equation for the solid metal is (ii) from 15 to 180 °C. Lithium which has

$$\rho_s/\Omega\ \mathrm{m} = 8{\cdot}685 \times 10^{-8} + 3{\cdot}261 \times 10^{-10}\theta_c + 1{\cdot}821 \times 10^{-13}\theta_c^2 \qquad \text{(ii)}$$

been purified by filtration followed by gettering with titanium and yttrium at 480 °C has the lowest resistivity. Less-elaborate methods of purification produce metal with a higher resistivity. For the liquid, $d\rho/d\theta_c$, though positive, decreases with increasing temperature, whereas for the solid, it increases with increasing temperature.

THE chemical and physical properties of lithium are currently under scrutiny due to the possible use of the liquid element as a combined source of tritium and coolant in future fusion reactors. The liquid is a versatile solvent for non-metals and the chemical reactions of dissolved solutes, one with another and with containment materials, are of practical and academic interest. The solubility of solutes and their chemical reactions can be determined by changes in the electrical resistivity of the solutions. In preparation for such studies, the resistivity has been determined of liquid and solid lithium from which the common impurities have been removed

EXPERIMENTAL

Apparatus and Procedure.—The apparatus (Figure 1) was constructed from stainless steel (AISI type 321), which is reputed to withstand attack by liquid lithium at the temperatures concerned.[1] A cylindrical reservoir, (A) (0·110 m long, 0·070 m diameter), contained the majority of the liquid metal. The reservoir was equipped with a neck, (B) (0·160 m long, 0·010 m diameter), for attachment to a vacuum frame through a glass-to-metal seal. The temperature of the reservoir was measured by means of a thermocouple situated in a pocket below the level of the liquid, (T_1). Another tube, (C) (0·200 m long, 0·040 m diameter), protruded into the top of the reservoir and was also attached to the vacuum frame. This tube was closed at its lower end by a sintered steel pad, (S) (Sintered Products Ltd., porosity 3). The essential features of the capillary loop (0·300 m long) and electromagnetic pump, (P), have been described previously.[2] By passing a direct current at right angles to a magnetic field through the pump duct, the liquid metal was drawn down from the reservoir. The resistance across the length, (R), of the capillary was measured by means of a Kelvin–Wheatstone double bridge. Thermocouples at (T_2) and (T_3) were used to measure the temperature of the capillary and hence the lithium under test.

The vessel was cleaned internally and dried as before.[3] It was mounted in a heated cabinet, the temperature of which could be controlled to $\pm\frac{1}{2}$ °C at 400 °C, and attached at the top to the vacuum frame. The vessel was evacuated, the temperature raised, and the resistance across the empty capillary was measured at selected constant temperatures. The apparatus was then cooled and charged with partially purified lithium under an argon atmosphere in a glove-box. Lithium was supplied in ingots (Koch–Light, 99·8%) protected by liquid paraffin and covered by a surface film of impurity. The oil was removed with petrol and the petrol distilled off under reduced pressure. The surface layer was then cut off in the glove-box. Clean lustrous pieces of metal were loaded (40 g) into the filtration tube, (C), and the apparatus

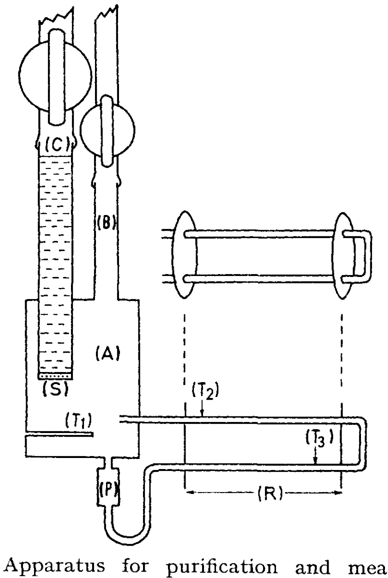

FIGURE 1 Apparatus for purification and measurement of resistivity of lithium; a perspective view of the capillary is also shown and tube (C) is charged with liquid lithium immediately prior to filtering

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[1] J. O. Cowles and A. D. Pasternak, UCRL-50647, 1969.

[2] C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, *J. Chem. Soc.* (*A*), 1971, 1393.

[3] C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, *J. Chem. Soc.* (*A*), 1969, 1482.

reassembled on the vacuum frame. Both sides of the filter were evacuated and the temperature raised to 190 °C to melt the lithium (m.p. 180·50 °C). Argon was admitted above the liquid, which was forced through the filter into the reservoir (A). This method of filtering lithium *in situ* eliminates a handling step and thereby preserves the purity of the filtered metal. On raising the temperature to 480 °C the lithium wetted the steel and flowed into and completely filled the capillary loop. This was accompanied by a large decrease in resistance which could be used, therefore, to follow the filling process. The pump was used to maintain uniformity of temperature in the metal and to provide continuous sampling through the capillary. The resistance of the filled capillary was measured at constant selected temperature down to 15 °C and equilibrium values of the resistivity of the liquid were calculated as before.[3]

Three variations in the above preparation of lithium were employed. (*i*) Freshly cut lithium was melted into the vessel without filtering. Two experiments were made with metal of starting purity 99·85 and 99·98% respectively. The specification for the latter was as follows (quantities in atom %); N, 0·009; Na, 0·009; K, 0·006; Cl, 0·006; (Al, Ca, Co, Cr, Cu, Fe, Ni, Si, O), $<0·002$. Although the specification showed relatively small amounts of non-metals, this was for interior samples and did not include the surface skin. (*ii*) Titanium sponge (5 g, Koch–Light, 99·9%) was immersed in filtered lithium (99·98%) and the liquid circulated over the getter at 480 °C for 48 h. (*iii*) Yttrium sponge (5 g, Koch–Light, 99·9%) was introduced in addition to the titanium and the gettering process was repeated.

RESULTS AND DISCUSSION

Resistivities of the Liquid and Purification.—The effect of temperature on the resistivity of liquid lithium purified by each of the three processes described above is shown in Figure 2. Metal which was most extensively purified by filtration followed by gettering by titanium and yttrium had the lowest resistivity [curve (*a*)]. The resistivity of this sample was lower than for any previously reported, but only marginally so for that gettered with zirconium by Shpil'rain (see later). The resistivity increased with increasing temperature; the temperature coefficient, $d\rho/d\theta_c$, though positive, decreased with increasing temperature. The resistivity was described precisely by equation (1) over the temperature range 180—460 °C.

$$\rho_l/\Omega\ \mathrm{m} = 16·476 \times 10^{-8} + 4·303 \times 10^{-10}\theta_c - 2·297 \times 10^{-13}\theta_c^2 \quad (1)$$

Metal (99·85%) which was merely washed and cleaned of surface impurity possessed the highest resistivity [curve (*d*)], presumably since the impurity level was highest in this sample. On using the same preparative procedure but starting with purer metal (99·98%), the resistivity was lowered to curve (*c*). The resistivity of metal which was only filtered but *in situ* was as low as for that which was subsequently further treated with titanium [curve (*b*)]. Gettering by yttrium after titanium produced only a further marginal decrease ($0·10 \times 10^{-8}$ Ω m) in resistivity. The most striking effect was the change ($0·7 \times 10^{-8}$ Ω m) caused by filtering the metal just above its melting temperature [*cf.* curves (*c*) and (*b*)]. This is a surprisingly effective way of reducing those impurities which result from contact of the metal with the atmosphere, *e.g.* Li_3N, Li_2O, LiOH, and perhaps Li_2CO_3 and Li_2C_2, even though the filtration method may be somewhat less effective for lithium than for sodium since the solubilities of non-metals are generally greater in liquid lithium near its m.p. (180·50 °C) than in sodium near its m.p. (97·8 °C).

Whether or not dissolved non-metals are removed from liquid lithium by a getter is governed by the difference in free energies of formation of the lithium and corresponding transition-metal compound. Values of $\Delta G_f^\ominus$ (kJ mol^{-1} non-metal) at 480 °C for some relevant compounds are given in Table 1. These values suggest that titanium is able to reduce Li_3N and Li_2C_2 to metallic lithium, but not Li_2O nor LiH. Yttrium appears capable of removing oxygen, nitrogen, hydrogen, and probably carbon from lithium (data for yttrium carbide are not available.)

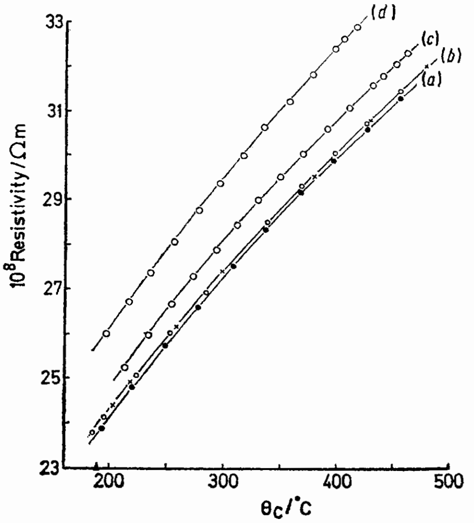

FIGURE 2 Variation of the resistivity of liquid lithium with temperature. (▲), M.p. of lithium

TABLE 1

Compound	$\Delta G_f^\ominus$ / kJ mol^{-1}	Ref.	Compound	$\Delta G_f^\ominus$ / kJ mol^{-1}	Ref.	Compound	$\Delta G_f^\ominus$ / kJ mol^{-1}	Ref.
Li_2O	−489	5	TiO	−451	1	Y_2O_3	−508	5
Li_3N	−96	1	TiN	−268	1	YN	−228	5
Li_2C_2	−54	1	TiC	−176	1			
LiH	−36	*	TiH_2	−15	*	YH_2	−50	*
			TiO_2	−387	5			

* Data from G. G. Libowitz, ' The Solid State Chemistry of Binary Metal Hydrides,' W. A. Benjamin, New York, 1965.

On the basis of these values, the difference in resistivity ($0·10 \times 10^{-8}$ Ω m) between curves (*a*) and (*b*) in Figure 2 may be attributed to dissolved oxygen and hydrogen, which titanium is unable to remove. The difference cannot be due to oxygen alone, since the unit increase in resistivity [$2·1 \times 10^{-8}$ Ω m (atom % O)$^{-1}$][4] is very

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[4] M. N. Arnol'dov, M. N. Ivanovskii, V. I. Subbotin, and B. A. Shmatko, *Teplofizika Vysokikh Temperatur*, 1967, **5**, 812.

small, and more oxygen than could saturate the liquid would be necessary to achieve the observed difference. Dissolved lithium hydride, however, had a much larger effect [$3{\cdot}8 \times 10^{-8}$ Ω m (atom % H)$^{-1}$],[4] and the difference is probably due largely to the presence of hydrogen which is subsequently removed by the yttrium. The large drop in resistivity from curve (*c*) to (*b*) (Figure 2) achieved by filtering is probably due largely to removal of nitrogen as solid Li_3N. The latter [5] is more soluble than Li_2O [5] and neither Li_2O nor LiH increase the resistivity of lithium by as much as does Li_3N [$7{\cdot}3 \times 10^{-8}$ Ω m (atom % N)$^{-1}$].[4]

The magnitude of the resistivity provides a sensitive measure of the purity of the liquid and, under the appropriate conditions, could be used to monitor continuously the liquid for contamination, especially by non-metals.

Depression of Freezing Point.—To examine the possibility that the metal samples could have contained a quantity of impurity to which the resistivity was insensitive, freezing points were determined from temperature–time curves, and are recorded in Table 2.

TABLE 2

Freezing points (°C) of lithium samples

(*i*) Filtered, gettered with Ti and Y	180·50
(*ii*) Cleaned of surface impurity only	180·34
(*iii*) As in (*i*) but subsequently saturated with N	180·10

The m.p. of lithium has been variously reported as between 176 and 180·5 °C with isolated and more dubious values at 185 °C depending on the purity.[6] Lithium which had the highest m.p. (180·50 °C) in our experiments (Table 2) also had the lowest resistivity, and the Table also shows that the freezing point increased with the degree of purification as expected. When dinitrogen was added, the trilithium nitride formed caused a small but significant drop (0·40 °C) in the freezing point. These results support our belief that the metal represented by curve (*a*) (Figure 2) is of high purity.

Resistivity of the Solid and the Change in Resistivity on Freezing.—On cooling the liquid to 180·50 °C, the metal solidified and the phase change was accompanied by an abrupt decrease in resistivity from $23{\cdot}50 \times 10^{-8}$ to $15{\cdot}10 \times 10^{-8}$ Ω m (Figure 3). The resistivities shown are equilibrium values obtained by holding the vessel at selected temperatures. By this means supercooling is avoided. The large increase (55·6%) in resistivity on melting is partly attributable to the transformation of the ordered body-centred-cubic structure of solid lithium to the largely disordered liquid. For the solid, the resistivity (Ω m) was given by equation (2) from 15 to 181 °C. In contrast to the liquid, $d\rho/d\theta_c$ for the solid, though still positive, increased with increasing temperature up to the m.p. The resistivity of both solid and liquid is relatively high and does not follow the smooth trend shown by the other alkali metals. The ratio $\rho_l : \rho_s$ (where ρ_l and ρ_s are the resistivities of the liquid and solid, respectively, at the m.p.) is similarly out of step despite the smaller volume change on melting for lithium. These quantities are shown in Table 3. Since all these metals should have the same resistivity at absolute zero temperature, we believe that the apparently anomalous high resistivity of liquid lithium is directly attributable to the disproportionately high value for the solid (caused by the relatively high field of the Li^+ ion) [7] which is augmented by the large ratio of $\rho_l : \rho_s$. If these effects are artificially removed then the resistivities of the liquid alkali metals increase progressively from lithium to caesium. This is shown in Figure 4 where the resistivity in excess of that at the m.p. is plotted against the corresponding excess of temperature for all five metals.

$$\rho_s = 8{\cdot}685 \times 10^{-8} + 3{\cdot}261 \times 10^{-10}\theta_c + 1{\cdot}821 \times 10^{-13}\theta_c^2 \tag{2}$$

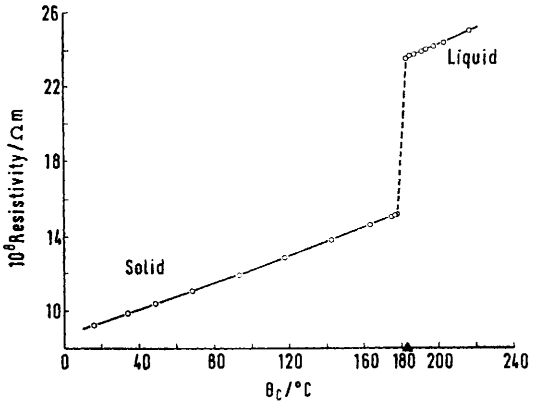

FIGURE 3 Variation of the resistivity of solid lithium with temperature and the change in resistivity on melting. (▲), M.p. of lithium

TABLE 3

Electrical resistivities (Ω m × 10^8) of the liquid (ρ_l) and solid (ρ_s) alkali metals at the m.p.

	Lithium		Sodium	Potassium	Rubidium	Caesium
ρ_l	23·49 [a]	24·25 [12]	9·67 [3]	13·52 [b]	22·75 [c]	36·0 [d]
ρ_s	15·16	15·29	6·80	9·36	14·70	21·7
$\rho_l : \rho_s$	1·55	1·59	1·42	1·44	1·55	1·66
Volume change on fusion [e] (% of solid volume)	1·65		2·50	2·55	2·50	2·60

[a] This work. [b] C. C. Addison, G. K. Creffield, and R. J. Pulham, *J. Chem. Soc.* (*A*), 1971, 2685. [c] S. M. Kapelner and W. D. Bratton, USAEC Report PWAC-376, 1962. [d] P. W. Bridgman, *Proc. Amer. Acad. Arts and Sci.*, 1921, **56**, 61; 1925; **60**, 285. [e] J. R. Wilson, *Met. Rev.*, 1965, **10**, 381.

Numerous theoretical values of ρ_l have been calculated from what is commonly known as Ziman's formula.[8] The results vary from $16{\cdot}0 \times 10^{-8}$ to $93{\cdot}3 \times 10^{-8}$ Ω m and the spread is due to the considerable uncertainty

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[5] E. E. Hoffman, USAEC Report ORNL-2894, 1960.

[6] R. P. Elliott, 'Constitution of Binary Alloys, First Supplement,' McGraw-Hill, London, 1965.

[7] O. Johnson, *Bull. Chem. Soc. Japan*, 1973, **46**, 1910.

[8] J. M. Ziman, *Adv. Phys.*, 1967, **16**, 421.

that exists on the best way to calculate the ionic pseudopotential and electron-scattering components of the

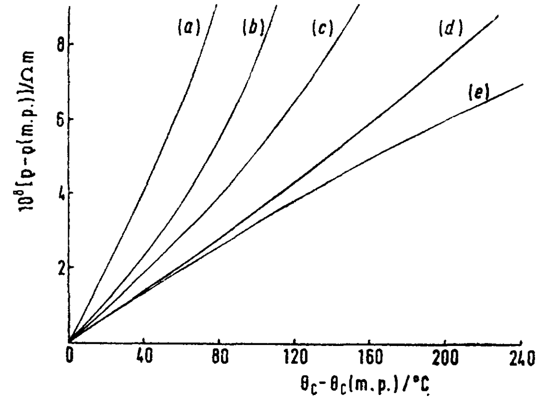

FIGURE 4 Variations of the resistivities of the liquid alkali metals with temperature: (*a*) and (*b*), Cs and Rb (S. M. Kapelner and W. D. Bratton, USAEC Report PWAC-376, 1962); (*c*), K [C. C. Addison, G. K. Creffield, and R. J. Pulham, *J. Chem. Soc.* (*A*), 1971, 2685]; (*d*), Na (ref. 3); and (*e*), Li (this work)

equation.[9] The closest agreement with the experimental result of $23{\cdot}49 \times 10^{-8}$ Ω m (Table 3) was obtained by Cubiotti *et al.* with a value of $23{\cdot}7 \times 10^{-8}$ Ω m.[10]

Temperature Coefficient of Resistivity.—An unusual feature of the resistivity of liquid lithium is the variation with temperature. The gradient, though positive, decreased with increasing temperature (Figure 4) in contrast to the other alkali metals. Indeed, lithium appears unique amongst all liquid metals in this respect. There is a trend, however, running through the alkali metals in the value of $d\rho/d\theta_c$, which progressively increases from lithium through to caesium (Table 4). For lithium there is an actual decrease with increasing temperature, whereas $d\rho/d\theta_c$ increases for potassium, rubidium, and caesium and the value for sodium is almost independent of temperature.

TABLE 4

$d\rho/d\theta_c$ Values (10^8 Ω m °C^{-1}) for the alkali metals

Li	Na	K	Rb	Cs	θ_c/°C
0·034	0·038	0·061	0·091	0·113	200
0·032	0·040	0·063	0·095	0·117	250
0·029	0·042	0·066	0·101	0·122	300

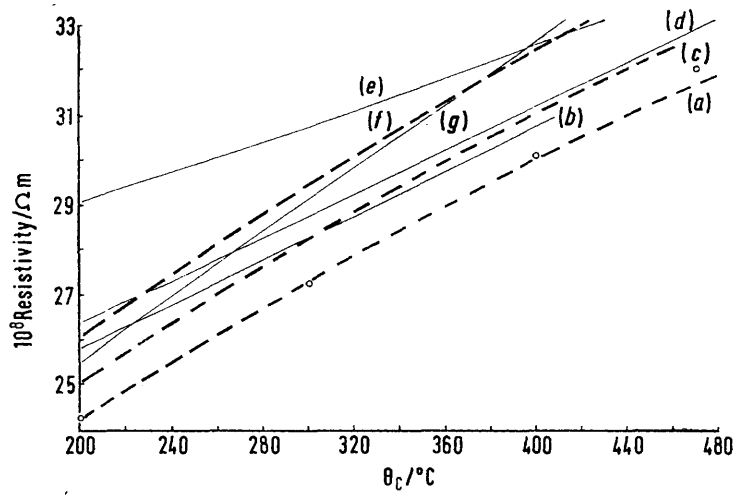

FIGURE 5 Summary of determinations of the resistivity of liquid lithium: (*a*), this work [(○), ref. 11]; (*b*), B. Yo. Semyachkin and A. N. Solov'ev, *Zhur. priklad. Mekhan. Tekh.*, 1964, **2**, 176; (*c*), J. F. Freedman and W. D. Robertson, *J. Chem. Phys.*, 1961, **34**, 769; (*d*) A. N. Solov'ev, *Zhur. priklad. Mekhan. Tekh.*, 1963, **1**, 158; (*e*) F. Roehlich and F. Tepper, *Electrochem. Technol.*, 1965, **3**, 234; (*f*), ref. 12; and (*g*), N. A. Vel'tishchev, Otchet ENIN no. 32, 1962.

Comparison with Previous Work.—Seven other determinations of resistivity have been published and are compared in Figure 5. Three main features are apparent: the present results [curve (*a*)] are the lowest; the various determinations differ in magnitude to a considerable extent; the temperature dependence of the resistivity varies widely between the determinations. Results which gave a similar gradient to that of curve (*a*) are shown as dashed lines. Values closest to curve (*a*) are those of Shpil'rain (circles);[11] these also would give a similar gradient. Two other determinations showed a variation with temperature similar to curve (*a*) but the resistivity was appreciably higher. In general the lowest resistivity values are given by metal which has undergone the most extensive purification. Of the non-metals likely to be present, nitrogen has the greatest effect on the resistivity and is most likely to be responsible for the observed discrepancies. Only two sets of data were accompanied by a nitrogen analysis, but the results support this belief. Thus, the metal used by Shpil'rain which gave low resistivity values was filtered and gettered with zirconium foil, and the

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[9] T. E. Faber, 'Introduction to the Theory of Liquid Metals,' Cambridge University Press, 1972, p. 329.

[10] G. Cubiotti, E. Guiliano, and R. Ruggeri, *Nuovo Cim.*, 1971, **B3**, 193; **B6**, 37.

[11] E. E. Shpil'rain and V. A. Savchenko, *Teplofizika Vysokikh Temperatur*, 1968, **6**, 254.

nitrogen content was $1{\cdot}2 \times 10^{-3}$ weight %. The metal used by Kapelner[12] was also gettered, but the nitrogen content rose to 0·23 weight % during the experiment; the resistivity was correspondingly high [curve (*f*)]. In all other determinations the metal was either used as supplied or no method of purification was described.

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[12] S. M. Kapelner, USAEC Report PWAC-349, 1961.