THERMOELECTRIC POWER OF AgI–Ag OXYSALT IONIC SOLIDS

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Summary

Thermoelectric power determinations carried out on the materials recently investigated as particularly suitable for the preparation of solid state galvanic cells allowed a comparison to be made between this family of compounds and the already studied $MeAg_4I_5$.

The possible interest of such materials for the direct conversion of thermal energy is finally examined with respect to the p-semiconductors on the basis of an evaluation of the figure of merit.

Introduction

In the last thirty years a large number of works have been devoted to the study of the thermoelectric power of ionic solids and melts. A comprehensive theoretical approach and a general literature review of this topic has been made by Wagner [1]. The principal aim of most of the works concerning ionic solids was to investigate the transport mechanisms and to evaluate the heats of transport of the point defects which had been recognized as existing in the lattice of the system considered [2 - 8]. The possibility of employing ionic solids in thermoelectric converters was incidentally examined by Christy [9] in a review concerning the thermoelectric power of "ordered" salts such as AgCl, AgBr, TlCl, pure and doped with divalent cations; in spite of the large values of the thermoelectric power of these materials (see Table 1), figures of merit not exceeding 10^{-4} deg^{-1} at 350 - 400 °C were evaluated, since the electric conductivity of these salts is quite low (thermal conductivity at these temperatures was estimated to be 10^{-3} W cm^{-1} deg^{-1}).

The special case of thermogalvanic cells containing α-AgI was considered by Weininger [10] who evaluated at 350 °C a figure of merit and an efficiency as large as 10^{-3} deg^{-1} and 5.1% (for an iodine electrode thermocell) respectively; in the same work some suggestions were given for a practical use of such cells as thermoelectric converters.

TABLE 1

Thermoelectric power data of some ionic solids. α-AgI and the family $MeAg_4I_5$ have highly disordered cationic sublattices, whereas the other salts in this Table are "ordered" solids having low concentrations of point defects. The temperature, T, reported in the equations of the second column is in K

Ionic solid	$-\epsilon$ (mV deg^{-1})	Temperature (°C)	Ref.
NaCl	$944/T - 2.295$	450 - 750	5
NaBr	1.1	600 - 700	6
KCl	1.8 - 1.9	550 - 700	4
KBr	1.8 - 1.9	500 - 700	6
AgCl	1.2	300	9
	0.9	350	8
AgBr	0.8	300	9
	0.6	350	8
γ-AgI	0.6	25 - 146	20
β-AgI	1.0	146	20
α-AgI	0.7	148	20
$RbAg_4I_5$	$93/T + 0.36$	25 - 200	17
KAg_4I_5	$78/T + 0.28$	25 - 200	17
$NH_4Ag_4I_5$	$58/T + 0.31$	25 - 200	17

The present work concerns thermoelectric power determinations on the ionic glass-like solids obtained by rapid quenching of molten $AgI-Ag_nXO_4$ (X = Cr, Mo, W, S, Se, Te, P, As) and $AgI-Ag_2Cr_2O_7$ mixtures having compositions of 75 - 80 mol% AgI (according to the particular system) which exhibit high ionic conductivity and seem suitable for manufacturing components of electronic devices [11 - 14].

The aim of these determinations is to examine the possibility of employing these materials in small thermoelectric converters and to attain a more reliable interpretation of their nature. A more extensive investigation was possible for the systems containing Ag_2SO_4, Ag_2WO_4 and Ag_3PO_4 which showed a satisfactory thermal stability: as a tentative conclusion it is suggested that such materials, though very similar in electrochemical performance to the compounds of the $MeAg_4I_5$ (M = Rb, K, NH$_4$) family, could not be considered strictly analogous to the latter in respect of the condition of the silver ions in their glass-like structure.

General considerations

It is well known that thermoelectric power investigations on ionic solids may sometimes give information about the order of magnitude of the heats of formation and migration of point defects; however, such conclusions may be drawn only when the solid considered and the type of point defects allow the entropy of the ionic species reversibly exchanging with

the electrode metal to be estimated through Pitzer's relation. This is the case
for thermocells such as: Ag/AgCl/Ag
$$T \qquad T + \Delta T$$
for which the thermodynamic expression of the thermoelectric power is

$$F\epsilon = S_{Ag} - S_{Ag^+} - Q^*_{Ag}/T = S_{Ag} - S^*_{Ag^+} \tag{1}$$

where F is the Faraday constant. Pitzer's relation cannot be applied to ionic
solids such as α-AgI and $MeAg_4I_5$ having "open lattice" structure, where it is
not possible to distinguish "defect" from "lattice" positions, to solids such
as γ-AgI where "chemical" disorder is superimposed on the "thermal" one
or finally to glassy materials, as considered here.

Therefore in these cases thermoelectric power data can give information
only on the value of the overall transported entropy:

$$S^*_{Ag^+} = F\epsilon - S_{Ag} \tag{2}$$

Some authors [15, 16] suggested that in the case of α-AgI, $RbAg_4I_5$ and
even $Ag_6I_4WO_4$ the difference $(S_{Ag} - S_{Ag^+})$ in eqn. (1) might be reasonably
considered constant over a wide temperature range, i.e. that where the
investigated material exists stably. Accordingly a linear fitting of the $F\epsilon$ vs.
$1/T$ curves should give a slope corresponding to Q^*_{Ag}. In the particular case
of $RbAg_4I_5$ it was roughly verified that such an assumption agrees with
a thermodynamical tentative estimation of S_{Ag^+} [16, 17].

In other cases it was claimed that for highly conducting ionic solids the
quantity Q^*_{Ag} should coincide with the activation energy evaluated from the
Arrhenius plot of the specific electric conductivity, σ. As a rule such conclu-
sions cannot be accurately verified as these ionic solids show quite small
(i.e. of the same order of magnitude as kT) activation energies and heats of
transport; accordingly uncertainties of 1 kcal/mol in the computation of the
activation energy values (e.g. from plotting $\log \sigma$ vs. $1/T$ instead of $\log \sigma T$
vs. $1/T$) would correspond to a 30 - 50% error.

Therefore for these ionic solids a comparison between Q^*_{Ag} values con-
tained in the thermoelectric power expression and the Arrhenius activation
energies drawn from a.c. conductivity data cannot be checked. Furthermore
Q^*_{Ag} and S_{Ag^+}, though not directly measurable, are thermodynamically well
defined quantities, whereas the "activation" energy is generally an empirical
parameter which has a reliable and satisfactory physical interpretation only
when "ordinary" solids are considered [18]. Therefore eqn. (2) is the only
relation which may be surely employed in working out the $F\epsilon$ data obtained
from these "disordered" solids.

Experimental

The procedure for the preparation of the AgI–Ag oxysalt materials has
been previously described as well as the experimental apparatus for the
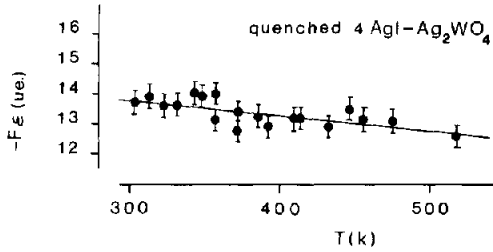determination of the thermoelectric power [12, 19, 20].

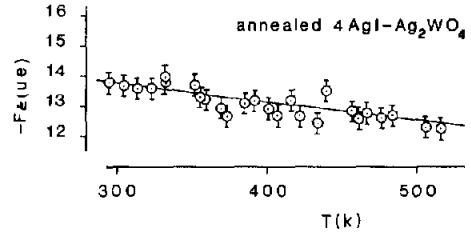Fig. 1. Thermoelectric power of the quenched $4AgI + Ag_2WO_4$ *vs. T.*

Fig. 2. Thermoelectric power of the annealed $4AgI + Ag_2WO_4$ *vs. T.*
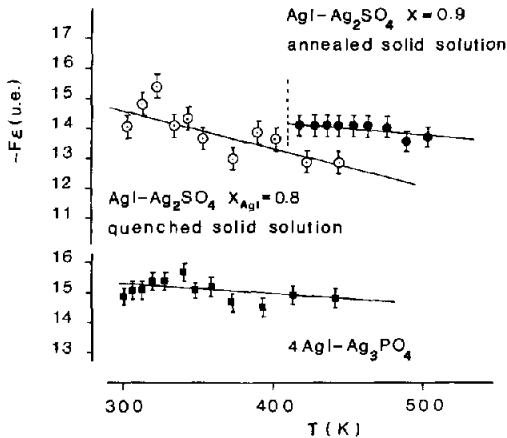

Fig. 3. Thermoelectric power of the solid solutions $AgI-Ag_2SO_4$, with $X_{AgI} = 0.8$ (quenched material) and $X_{AgI} = 0.9$, and of the quenched $4AgI + Ag_3PO_4$.

Results and Discussion

Figures 1 and 2 report the experimental $F\epsilon$ values for the system containing Ag_2WO_4 before and after an annealing procedure [19], respectively; the two kinds of materials differ in the extent of the crystal order and could be distinguished by Armstrong [21] by the behaviour of their complex impedance. In the present case differences are very small and it seems likely that the transport properties of the two "modifications" are quite similar (see also ref. 19).

Figure 3 reports the case of the systems containing Ag_3PO_4 and Ag_2SO_4 (the latter are solid solutions with $X_{AgI} = 0.8$ and 0.9): determinations were carried out until a "decomposition" or crystallization process occurred with consequent modification of the properties of the materials [19]. Thermoelectric power values were somewhat larger than those observed for the other systems considered in this work.
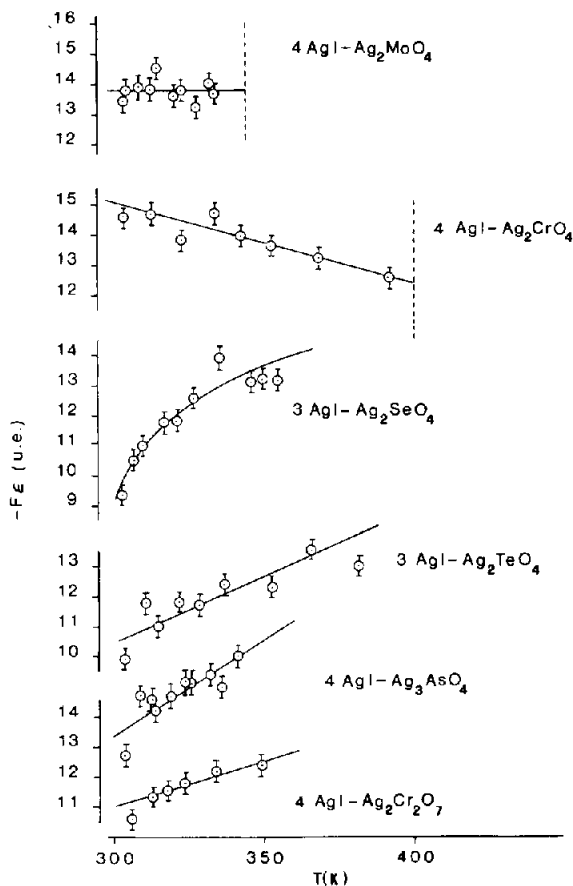
Fig. 4. Thermoelectric power of the quenched systems $AgI-Ag_2XO_4$ (X = Mo, Cr, Se, Te, As), with X_{AgI} = 0.8 or 0.75 according to the particular system, and of the quenched system $4AgI + Ag_2Cr_2O_7$.

As for the temperature dependence of the experimental data of these systems, it was verified, as expected, that it was negligible, (e.g. for $4AgI:Ag_2WO_4$ a Q^*_{Ag} less than 1 kcal/mol was obtained by plotting $F\epsilon$ vs. $1/T$).

Figure 4 reports the $F\epsilon$ values of the systems with lower thermal stability which were investigated over narrow temperature ranges: for some of these systems the values of thermoelectric power were close to those detected for $4AgI:Ag_2WO_4$ at room temperature.

In order to compare these materials with other silver ion conductors the quantities $S^*_{Ag^+}$ calculated according to eqn. (2) are given in Table 2.

It can be easily seen that the $S^*_{Ag^+}$ values referring to the glass-like materials lie below those for α-AgI and are 2 - 3 e.u. larger than those of the $MeAg_4I_5$ family. Assuming that for all the compounds listed in Table 1 the

TABLE 2

The overall transported entropy $S^*_{Ag^+}$ is reported for the AgI–Ag oxysalt materials as well as for α-AgI and the MeAg$_4$I$_5$ family (the latter reported from ref.17). Columns referring to the AgI–Ag oxysalt systems are labelled by the chemical symbol of the element present in the oxyanion; Cr$_2$ refers to the system AgI–Ag$_2$Cr$_2$O$_7$. Values reported for temperature ranges not investigated were obtained through a linear extrapolation of the experimentally determined values. Values are in entropic units.

T/K	α-AgI	RbAg$_4$I$_5$	KAg$_4$I$_5$	NH$_4$Ag$_4$I$_5$	W Quenched	W Annealed	Mo	Cr	P	$S(X_{AgI})$ 0.8	$S(X_{AgI})$ 0.9	Se	Te	As	Cr$_2$
300	28.2	23.3	22.4	21.8	24.0	24.0	24.0	25.1	25.5	24.8	25.1	24.1	20.4	21.3	25.2
325	28.1	23.4	22.7	22.0	24.5	24.5	24.5	25.1	26.0	25.1	25.6	24.9	22.1	22.8	25.6
350	28.0	23.3	22.7	22.2	24.8	24.7	24.9	24.9	26.3	25.2	25.8	25.5	23.7	24.1	25.8
375	28.0	23.4	23.0	22.3	25.1	25.0	25.3	24.8	26.7	25.4	26.2	26.2	25.3	25.5	26.1
400	27.9	23.5	23.1	22.5	25.4	25.3	25.7	24.7	27.0	25.5	26.4	26.8	26.8	26.8	26.3
425	27.8	23.5	23.2	22.7	25.7	25.5	26.0	24.5	27.3	25.6	26.7	27.4	28.4	28.1	26.4
450	27.7	23.7	23.3	22.9	25.9	25.8	26.0	24.3	27.6	25.7	26.1	27.9	29.9	29.4	26.6
475	27.6	23.7	23.3	23.0	26.1	25.9	26.6	24.0	27.8	25.8	27.1	28.4	31.3	30.6	26.7
500	27.6	23.9	23.4	23.2	26.4	26.2	27.0	23.8	28.1	25.9	27.3	29.0	32.8	31.9	26.9
525	27.5	24.0	23.5	23.4	26.6	26.3	27.2	23.6	28.3	25.9	27.5	29.5	34.3	33.1	26.9
550	27.4	24.1	23.5	23.6	26.7	26.4	27.4	23.3	28.5	25.9	27.6	30.0	35.7	34.3	27.0

transport term Q^*_{Ag}/T is essentially the same (at room temperature it ranges from 7 to 10 e.u.) it follows that the term S_{Ag^+} should also be equal (with an uncertainty of say ± 1.5 e.u.) for all of them; however, this term contains both vibrational and configurational contributions so that it is quite difficult at present to decide whether each one of these two contributions assumes the same value throughout the whole group of materials of Table 1 or whether an internal compensation occurs.

It can be only said that all the silver ions within the "open lattice" of $MeAg_4I_5$ ionic solids are equivalent to one another whereas this cannot be surely assumed for the AgI–Ag oxysalt materials.

Energy conversion

The ionic solids considered in this work, as well as those of the $MeAg_4I_5$ family, might also be considered as possible materials for the conversion of thermal energy; in fact they show a large thermoelectric power (500 - 600 $\mu V \ deg^{-1}$) as good as most of the ionic conductors and a good electric conductivity (10^{-1} - $10^{-2} \ ohm^{-1} \ cm^{-1}$); their thermal conductivity, κ, is not known, but it should not be as large as that of the usual semiconductors: assuming for κ the value reported [22] for α-AgI, *i.e.* $1 \times 10^{-1} \ W \ cm^{-1} \ deg^{-1}$, one can evaluate a merit figure

$$z_m = \frac{\epsilon^2 \sigma}{\kappa} = 10^{-3} \text{ - } 10^{-4} \ deg^{-1}$$

Such values of z_m are not equivalent to those reported for the best p semiconductors [23]; however, the higher voltages supported by these thermocells and their small dependence on T might suggest the application of these materials in thermoelectric devices in particular cases. The practical application of such thermocells is indeed seriously limited by the mass transfer at the electrodes, but a careful preparation of the latter which improves their behaviour with respect to polarization phenomena [12] should reduce this effect and so increase their field of application.

Such electrodes were prepared for solid state galvanic cells containing these materials; they were obtained by intimately mixing silver powder with the powdered salt, both having a main grain size of 70 μm, and resulted in an improvement of the discharge duration of the cell at a current density of 0.2 mA/cm^2 from a few minutes to ten hours.

It is obvious that, due to the low amount of thermal energy which could be converted by such ionic thermocells, they are not suitable as industrial converters, whereas it is possible to take them into consideration as microdevices for special electronic circuits.

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