

# Thermoelectric effects in electrochemical systems. Nonconventional thermogalvanic cells <sup>☆</sup>

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## Abstract

In the present study, the possibility of using electrochemical systems for solving the problems of direct thermoelectric conversion is considered for a number of nonconventional electrochemical couples: ‘inert’ electrode/macrocylic complex with the central coordinated metal ion in different oxidation states (aqueous, aprotic organic electrolyte), ‘inert’ electrode/metal ion in different oxidation states (molten salt), lithium intercalate/lithium-containing aprotic organic electrolyte, semiconductor/molten salt. A comparative analysis of data on the main criteria of thermoelectric ability (Seebeck coefficient, efficiency factor, Z-factor, efficiency, etc.) confirmed that it is possible in principle to use the electrochemical systems studied in direct thermoelectric conversion devices.

**Keywords:** Electrochemical systems; Thermogalvanic cells

## 1. Introduction

One of the promising trends in modern minor energetics is the development of direct thermoelectric conversion (DTEC) devices using electrochemical systems. Redox systems with ‘inert’ electrodes [1–12] are of special interest since they have a high Seebeck coefficient and a long service life. However, their disadvantages, such as the limited operating temperature range and the necessity to use noble metals as the electrode, restrain their practical realization.

In the present study, new types of electrochemical systems have been investigated, in which the thermogalvanic cell circuit has been given in Scheme 1.

## 2. Electrochemical systems

### 2.1. Thermogalvanic systems with aqueous solutions

2.1.1. Systems:  $Pt|xK_4Fe(CN)_6, yK_3Fe(CN)_6, H_2O$   
 $Pt|xK_4Fe(CN)_6, yK_3Fe(CN)_6, zKCl, H_2O$   
 $Pt|xFe_4Fe(CN)_6, yK_3Fe(CN)_6, zKNO_3, H_2O$

A typical dependence of thermal e.m.f. on temperature difference  $\Delta T$  between the ‘hot’ and ‘cold’ elec-

trode for an electrochemical system in the initial state is shown in Fig. 1.

In Ref. [4], we reported in detail experimental data on the above-mentioned systems and their interpretation. By analyzing the results obtained in terms of the possibility of using the system under consideration for DTEC, we can conclude that the maximum value of the thermoelectric coefficient  $\epsilon_{in}$  is attained at infinite dilution and is  $-1.803 \times 10^{-3}$  V/K; for an electrolyte concentration of over 0.2 M,  $\epsilon_{in}$  remains practically unchanged (about  $1.55 \times 10^{-3}$  V/K) (Fig. 2).

Such a variation of  $\epsilon_{in}$  with the electrolyte concentration is described by Eq. (1) [6]:

$$\epsilon_{in} = \epsilon_{in}^0 + 2.3(R/F) \ln \Pi_i(a_i) \quad (1)$$

where  $\epsilon_{in}^0$  is a quantity that is independent of the electrolyte composition and is typical of the given electrode;  $\Pi_i$  is the product sign and  $a_i$  is the activity of the electrolyte components.

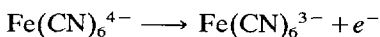
The applicability of Eq. (1) is supported by the fact that the experimental data fall satisfactorily on the straight line in the Debye–Hückel coordinates and that the slope of the experimental plot is close to the theoretical one ( $2.3 R/F = 0.2 \times 10^{-3}$  V/K) (1). Taking into account the signs and complex forms of the charge carriers of the system under consideration, the following

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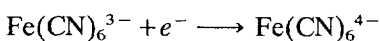
1.	A' end phase	A 'inert' electrode Pt, Cu	iron and copper complex compounds (aqueous solutions) $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ $\text{CuTAAB}^{2+}/\text{CuTAAB}^+$ $\text{Cu}(\text{fen})_2^{2+}/\text{Cu}(\text{fen})_2^+$ $\text{Cu}(\text{dipy})_2^{2+}/\text{Cu}(\text{dipy})_2^+$ 280–370 K	A 'inert' electrode Pt, Cu	A' end phase
	$T_{\square}$	$T_h$		$T_c$	$T_{\square}$
2.1.	A' end phase	A 'inert' electrode Cu	copper complex compounds (nonaqueous organic solutions) $\text{CuTAAB}^{2+}/\text{CuTAAB}^+$ $\text{Cu}(\text{dipy})_2^{2+}/\text{Cu}(\text{dipy})_2^+$ 230–470 K	A 'inert' electrode Cu	A' end phase
	$T_{\square}$	$T_c$		$T_h$	$T_{\square}$
2.2.	A' end phase	A $\text{Li}_x\text{TiS}_2$ ( $\text{Li}_x\text{FePS}_3$ ) intercalate	complex lithium salt in nonaqueous organic solvent 230–470 K	A $\text{Li}_x\text{TiS}_2$ ( $\text{Li}_x\text{FePS}_3$ ) intercalate	A' end phase
	$T_{\square}$	$T_c$		$T_h$	$T_{\square}$
3.1.	A' end phase	A 'inert' electrode Mo, W	Me+MeX melt $\text{Cd}^{2+}/\text{Cd}^+$ , $\text{La}^{3+}/\text{La}^{2+}$ $\text{LaCl}_6^{3-}/\text{LaCl}_4^{2-}$ 650–1500 K	A 'inert' electrode Mo, W	A' end phase
	$T_{\square}$	$T_c$		$T_h$	$T_{\square}$
3.2.	A' end phase	A semiconductor	$\text{BiCl}_3(x)+$ $\text{AlCl}_3-\text{NaCl}-\text{KCl}$ melt 400–620 K	A semiconductor	A' end phase
	$T_{\square}$	$T_c$		$T_h$	$T_{\square}$

Scheme 1.

scheme of electrode reactions, that can take place on the 'hot' and 'cold' electrodes of the thermocell when a current traverses it, may be suggested:



on the 'hot' electrode



on the 'cold' electrode

The liquid thermoelectric material (LTM) studied can be compared with materials proposed for use in thermoelectric converters by means of the so-called Z-

factor (figure-of-merit) [13–18]:

$$Z = \frac{\epsilon^2}{\{(\rho_A \lambda_A)^{1/2} + (\rho_B \lambda_B)^{1/2}\}^2} \quad (2)$$

where  $\rho_A$  and  $\rho_B$  are the specific resistances and  $\lambda_A$  and  $\lambda_B$  the heat conductivities of the electrode and electrolyte, respectively. The Z-factor can be calculated from data in Ref. [19] for relatively dilute solutions (up to 0.1 M), though the working concentrations for known LTMs reach several moles per litre. However, even when these data are used, the Z-factor for the system under consideration is several times higher than that for thermocells with reversible electrodes. Thus,

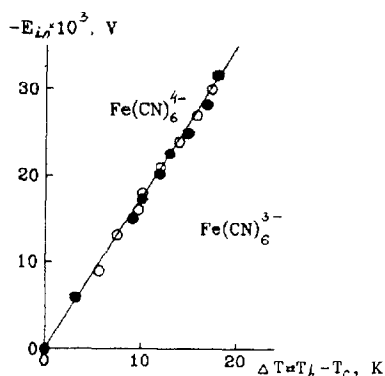


Fig. 1.  $E_{in}$  of the electrochemical system  $Pt|xFe(CN)_6^{4-}, yFe(CN)_6^{3-}, H_2O|Pt$  as a function of the temperature difference between the 'hot' ( $T_h$ ) and 'cold' ( $T_c$ ) electrodes: (1,2) forward and return run, respectively,  $T_c = 298$  K,  $x = y = 0.015$  M;  $\epsilon_{in} = \Delta E_{in} / \Delta T = -1.666 \pm 0.006 \times 10^{-3}$  V/K;  $\circ$ —1,  $\bullet$ —2.

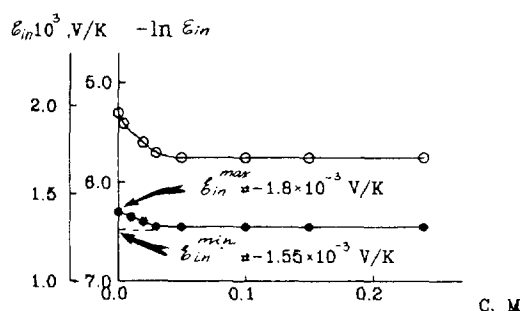


Fig. 2. Coefficient of initial thermal e.m.f., ( $\bullet$ )  $\epsilon_{in}$  and ( $\circ$ )  $\ln \epsilon_{in}$  as a function of electrolyte concentration. Electrochemical system.  $Pt|xK_4Fe(CN)_6, yK_3Fe(CN)_6, zKCl, H_2O|Pt$ ; concentration  $= x = y = z = 0.0$ – $0.3$  M;  $T = 293$ – $368$  K.

for instance, the Z-factor for the thermocell,  $Pt|0.1$  M  $K_4Fe(CN)_6, 0.1$  M  $K_3Fe(CN)_6, H_2O|Pt$ , is  $1 \times 10^{-5}$   $K^{-1}$ . If we take into account that  $\kappa$  may reach values of the order of 20 S/m for working LTM concentrations, the Z-factor is about  $0.2 \times 10^{-3}$   $K^{-1}$ , which is one order of magnitude higher than for a system with reversible electrodes (see Table 1).

Thus, by analyzing the characteristics given in Table 1 and taking into account the fact that a thermoelectric converter based on the redox system, under consideration, will have an actually unlimited service life, one can conclude that it is expedient to use this system in DTEC devices [20–22]. It should be also noted that the electrochemical redox system considered has been thoroughly studied for use as the positive electrode in direct chemical-to-electric energy conversion devices (concentration power sources) [23,24].

### 2.1.2. Systems: $Cu|xCuTAAB(NO_3)_2, yCuTAAB(NO_3)_3, H_2O|Cu$ $Cu|xCu(2,2'-dipy)_2Cl_2, yCu(2,2'-dipy)_2Cl, H_2O|Cu$

An analysis of the literature on the synthesis, physicochemical properties and application [25–30] of or-

ganometallic compounds allowed us to conclude that these materials can be used as electroactive components in DTEC devices. The application of compounds of such as liquid thermoelectric materials based on redox systems is promising for the following reasons. Owing to the metal ion being firmly held by the ligand, relatively inexpensive nonferrous metals (copper, stainless steel) can be used as 'inert' electrodes in such systems. This would substantially lower the cost of the electrode material on the one hand and allow a highly extended electrode surface to be obtained and hence the power characteristics of thermoelectric devices to be improved on the other hand.

The copper complexes with organic ligands considered in this section were synthesized by the methods reported in Refs. [25,26]. The system under investigation was prepared by dissolving electroactive substances (copper complexes with organic ligands) in double-distilled water or in a potassium chloride-based electrolyte. A platinum or copper wire of  $2 \times 10^{-3}$  m diameter served as an 'inert' electrode. The coefficients of initial thermal e.m.f. were measured and calculated like those of the above systems. Fig. 3 shows a typical dependence of initial thermal e.m.f.,  $\epsilon_{in}$ , on the temperature of the 'hot' electrode,  $T_h$ .

The concentration dependences of the systems studied at an electroactive redox species ratio of 1:1 are similar to those shown in Fig. 3.  $\epsilon_{in}^{max}$  and  $\epsilon_{in}^{min}$  calculated from these data are listed in Table 1 together with other energy parameters.

Taking into account the experimental data, we concluded that the heat and electrotransfer processes in these systems and in an iron-ferro-ferrocyanide-based system are identical and that Eq. (1) can be used for their description.

## 2.2. Thermogalvanic systems with nonaqueous organic solutions

### 2.2.1. Redox systems with 'inert' electrodes

The use of transition metal complexes with organic ligands as electroactive LTM components makes it possible, in addition to the advantages cited in Section 2.1., to extend considerably the temperature range. Many organometallic compounds are rather readily soluble in organic solvents, which opens a possibility to develop on their basis LTMs with a wider operating temperature range (230–470 K).

To check the use of such a nonconventional type of electrochemical system in DTEC devices and to study the effect of nonisothermality on them, we used circuits whose phase schemes are given in Section 1. The choice of nonaqueous organic solvents was determined by the temperature range of the liquid state and by the solubility of electroactive substances in those solvents. The following aprotic organic solvents were chosen: acetonitrile



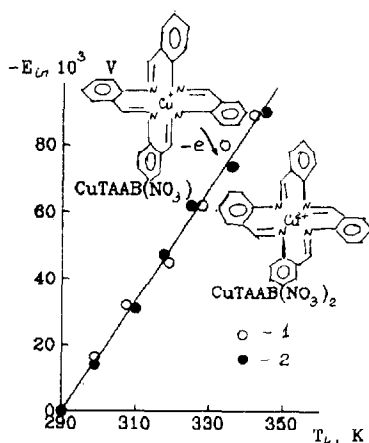


Fig. 3. Initial thermal e.m.f.,  $E_{in}$ , of the electrochemical system  $Cu_xCuTAAB(NO_3)_2, yCuTAAB(NO_3), H_2O|Cu$  as a function of 'hot' electrode temperature,  $T_h$ : (1,2) forward and return run, respectively;  $T_c = 293$  K;  $x=y=1 \times 10^{-6}$  M;  $\epsilon_{in} = \Delta E_{in}/\Delta T = -(1.86 \pm 0.02) \times 10^{-3}$  V/K.

(AN), dimethyl sulfoxide (DMSO), dimethylformamide (DMFA) and  $\gamma$ -butyrolactone ( $\gamma$ -BL) (see Table 2). The LTMs under investigation were prepared by dissolving  $CuTAAB(NO_3)_2$  and  $CuTAAB(NO_3)$  or  $Cu(2,2'$ -dipy) $_2Cl_2$  and  $Cu(2,2'$ -dipy) $_2Cl$  in an appropriate solvent or electrolyte. The solvents were purified by methods described in Refs. [27,28]. The 'inert' electrodes were a platinum or copper wire of  $2 \times 10^{-3}$  m diameter. There was no change in the working electrode mass after long measurements (up to 12 h with changing the temperature difference towards higher and lower values), i.e., there was no electrode mass transfer. The coefficients of initial thermal e.m.f. were measured and calculated as in Ref. [4]. The dependences of initial thermal e.m.f. on the 'hot' electrode temperature were linear, and the residual thermal e.m.f. (at  $\Delta T=0$ ) was close to zero.

Table 2

Values of the coefficient of initial thermal e.m.f. for electrochemical systems based on nonaqueous organic solvents (L) and some properties of these solvents:  $x=y=1 \times 10^{-6}$  M;  $z=j=1 \times 10^{-3}$  M

Solvent, electrolyte L	Melting point $T_m$ (K)	Boiling point, $T_b$ (K)	Operating temperature (K)	Dielectric constant	Cutman acceptor number	Coefficient of initial thermal e.m.f. $\epsilon_{in} \times 10^3$ (V/K)
a) System $Cu_xCuTAAB(NO_3)_2, yCuTAAB(NO_3), L Cu$						
DMFA	212	426	214	36	16	$0.17 \pm 0.02$
$\gamma$ -BL	229	477	248	39		$0.45 \pm 0.01$
DMSO	292	462	170	45	19	$0.76 \pm 0.03$
AN	227	355	128	38	19	$0.94 \pm 0.03$
$H_2O$	273	373	100	81	55	$1.86 \pm 0.02$
1 M $LiBF_4$ in $\gamma$ -BL			240			$0.34 \pm 0.03$
b) System $Cu_zCu(2,2'$ -(dipy) $_2Cl_2, jCu(2,2'$ -dipy) $_2Cl, L Cu$						
1 M $LiBF_4$ in $\gamma$ -BL			240			$4.17 \pm 0.2$

Fig. 4 shows the effect of the ratio of the reduced and oxidized forms of potential-determining macrocyclic copper ions on the coefficient of initial thermal e.m.f. The highest thermoelectric coefficient value is attained at  $C_{CuTAAB(NO_3)} \rightarrow 0$ .  $\epsilon_{in}$  decreases monotonically to a value of the order of  $-0.45 \times 10^{-3}$  V/K at  $\rho=1$  with increasing concentration of  $CuTAAB(NO_3)_2$ . Such a variation of  $\epsilon_{in}$  can be explained as follows.

The equilibrium potential  $\phi_{eq}$  of an 'inert' electrode immersed in the LTM under investigation will be determined by the redox potential of the electrode reaction:



and can be described by the Nernst equation:

$$\phi_{eq} = \phi_{eq}^0 - 2.3 \frac{RT}{F} \log \frac{a_{CuTAAB^+}}{a_{CuTAAB^{2+}}} \quad (4)$$

where  $a_{CuTAAB^+}$  and  $a_{CuTAAB^{2+}}$  are the activities of the potential-determining macrocyclic copper complexes in an appropriate solvent.

Making use of the approach reported in Ref. [6] and assuming the second Thompson relation that will be also applicable to the new class of LTMs under consideration, we obtain the following approximate expression for the coefficient of initial thermal e.m.f.:

$$\epsilon_{in} = \epsilon_{in}^0 - 2.3 \frac{R}{F} \log \frac{a_{CuTAAB^+}}{a_{CuTAAB^{2+}}} \quad (5)$$

The applicability of Eq. (5) to the type of LTMs under consideration based on nonaqueous organic electrolytes is supported by the fact that — as follows from Fig. 4

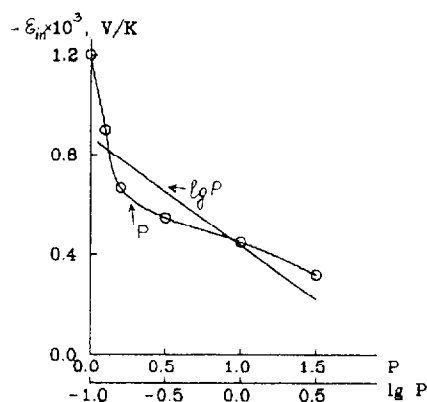


Fig. 4. Coefficient of initial thermal e.m.f.,  $\epsilon_{in}$ , of the electrochemical system  $\text{Cu}_x\text{CuTAAB}(\text{NO}_3)_y$  as a function of the ratio of the reduced and oxidized forms of electroactive substances.  $P = x/y$ ,  $x = 1 \times 10^{-6} - 1 \times 10^{-5}$  M,  $y = 1 \times 10^{-6} - 1 \times 10^{-5}$  M.

– the experimental data fall satisfactorily on the straight line in the semilogarithmic  $\epsilon_{in} - \log P$  coordinates, and the slope of the experimental plot is close to its calculated value ( $2.3 R/F = 0.2 \times 10^{-3}$  V/deq).

Thus, Eq. (5) described qualitatively the experimental data obtained, allowing one to assume the following scheme of electrode reactions that occur on the electrodes of a thermocell when a current traverses it:  $\text{CuTAAB}^+ \rightarrow \text{CuTAAB}^{2+} + e^-$  on the ‘hot’ electrode;  $\text{CuTAAB}^{2+} + e^- \rightarrow \text{CuTAAB}^+$  on the ‘cold’ electrode. It follows that the overall reaction for the electrochemical system of the thermocell under consideration reduces to diffusive  $\text{CuTAAB}^+$  transfer from the ‘cold’ electrode to the ‘hot’ one and that heat is transferred in the opposite direction.

From the afore-said it can be concluded that the scheme of heat and mass transfer processes in the redox system based on nonaqueous organic media is the same for similar systems based on aqueous solutions and ideal ionic melts [3,4,6,29–31]. This identity seems to be due to the presence of a solvent (protic solvent–water or aprotic solvent–organic solvent, salt melt) in all thermocells under consideration having redox systems.

Comparison of systems with different solvents (Table 2) allows one to conclude that the coefficient of initial thermal e.m.f. correlate to a certain extent with the dielectric constant and Gutman acceptor number [32], which makes it possible to select, in advance, nonaqueous organic solvents on the basis of their physicochemical properties and the purpose of LTM.

Tests of thermocell mock-ups based on electrochemical systems with nonaqueous organic electrolytes showed that they have a high serviceability, high operating characteristics (power, short-circuit current, Z-factor, efficiency) and that it is possible in principle to use these thermocells over a broad temperature range.

## 2.2.2. Systems with electrodes based on intercalated structures

We have also realized, in nonaqueous organic media, a nonconventional electrochemical system with electrodes based on a new class of materials for energy conversion systems, namely intercalated ‘host-guest’ structure or intercalation compounds.

To check experimentally the serviceability of such a type of electrochemical system and to study the effect of temperature gradient and ‘guest’ lithium concentration in the ‘host’ structure on the characteristics of the thermocell, we used the circuit whose phase scheme is given in Section 1.

The use of a solution of a lithium salt in a nonaqueous organic solvent makes it possible to use the most energetic metal–lithium as electroactive component and to broaden the operating temperature range of the thermocell. The use of lithium-intercalated structures (e.g.,  $\text{TiS}_2$ ,  $\text{FePS}_3$ ,  $\text{NiPS}_3$ ) provides, in addition to high power, the possibility to cycle the thermocell, whereas a pure-lithium electrode immersed in a solution of a lithium-containing salt in an aprotic organic solvent cannot be cycled repeatedly due to the electrode surface being blocked by an oxide film and dendrite formation.

The data obtained for the system  $\text{Li}_x\text{TiS}_2/\text{LiBF}_4$  in  $\gamma\text{-BL}/\text{Li}_x\text{TiS}_2$  are listed in Table 3. As follows from the analysis of the data obtained, LTM based on the electrochemical system studied possesses a high thermoelectric power, a broad operating temperature range and a long service life (up to 100 cycles). A thermocell based on this material has fairly high power characteristics due to the high voltage and current values. The power of such a thermocell is by one order of magnitude higher than that of the thermocell with an aqueous electrolytic solution and reversible metal electrodes.

Table 3  
Characteristics of thermocells based on the electrochemical system  $\text{Li}_x\text{TiS}_2/\text{LiBF}_4$  in  $\gamma\text{-BL}/\text{Li}_x\text{TiS}_2$ ;  $\Delta T = 60$  K

Electrode concentration $\text{Li}_x$ in $\text{Li}_x\text{TiS}_2$ (wt.%)	Electrolyte (wt.%) $\text{LiBF}_4$	$\gamma\text{-BL}$	$\epsilon_{in} \times 10^3$ (V K <sup>-1</sup> )	$I_{SC} \times 10^6$ (A)	$E \times 10^3$ (V)	$P \times 10^3$ (W m <sup>-2</sup> )
0.6	52	48	0.65	16	46	28
1.3	52	48	0.79	16	56	33
3.0	52	48	2.02	67	116	300
3.6	52	48	4.62	83	276	892
4.5	52	48	1.85	53	111	230
5.3	52	48	1.29	36	90	126
3.6	36	64	3.84	71	201	553
3.6	22	78	3.06	52	141	287

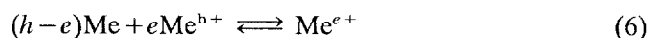
### 2.3. Thermogalvanic systems with salt melts

A considerable success in solving DTEC problems can be also achieved by utilizing the advantages of salt melts (as ionic liquids) over conventional aqueous electrolytic solutions. These advantages include, above all, the fact that the rate of current-producing processes and, hence, the current density in ionic melts are much higher than in aqueous and nonaqueous organic solutions, which results in a higher specific power of energy converter (Table 4).

#### 2.3.1. Redox systems with 'inert' electrodes

The thermoelectric properties of systems based on salt melts and their mixtures on reversible solid, liquid and gas electrodes have been well studied; there are no similar studies on redox systems with 'inert' electrodes [34–37].

The current-producing process in such systems is caused by redox reactions or 'recharge' reactions proceeding at electrodes with electron transition between metal ions in different oxidation states. In molten media, such systems are realized when a metal is readily soluble in its molten salt to form species of different valences. In this case, the following equilibrium is established:



where  $h$  is the number of electrons of the highest valence ion and  $e$  the number of electrons of the lowest valence ion.

A detailed study of various physicochemical properties of the systems under discussion showed that all of them can be divided into two classes: 'metallic' solutions of metals and 'nonmetallic' solutions of metal [38–41].

Table 4  
Electrical conductivity  $\kappa$  of commercially important ionically conducting systems (from Ref. [33])

System	Temperature (K)	$\kappa \times 10^2$ (S m <sup>-1</sup> )
2.81 M LiClO <sub>4</sub> /H <sub>2</sub> O	298	1517
2.84 M LiClO <sub>4</sub> /H <sub>2</sub> O	273	878.4
LiI <sub>(solid)</sub>	298	$1 \times 10^{-3}$
LiI/Al <sub>2</sub> O <sub>3</sub>	573	50–500
Li <sub>3</sub> N	298	10
LiCl <sub>(liquid)</sub>	910	58540
LiCl(58.5 mol%)-KCl <sub>(eutectic)</sub>	748	16150
0.66 M LiClO <sub>4</sub> /PC	298	54.2
0.34 M LiClO <sub>4</sub> /PC	228	2.75
1.39 M LiClO <sub>4</sub> /PC(42 wt.%), DME	298	145.9
0.74 M LiClO <sub>4</sub> /PC(28 wt.%), DME	228	33.1
LiBr/An, SO <sub>2</sub>	298	500
LiBr/An, SO <sub>2</sub>	223	240

PC: propylene carbonate; DME: dimethoxyethane; AN: acetonitrile.

The first class includes solutions of alkali, alkaline-earth and rare-earth metals in their molten salts. Such systems are characterized by a high solubility of the metals, a high electrical conductivity which decreases with temperature and an increase in solubility with increasing metal vapour pressure. They possess a 'metallic' conductivity. This class of 'metallic' solutions of metals is best described by the ionic–electronic liquid theory [42].

The second class includes all the other solutions of metals in their molten salts. They are characterized by ionic conductivity which increases with temperature and by a decrease in the solubility of the metal on adding some foreign salts. Such systems are best described by the subcompound formation theory.

There are various views as to the composition of ions arising from the formation of subcompounds. This question should be apparently solved for each particular case, as will be shown below in the discussion of the experimental results in previous work [3,6,29].

#### 2.3.1.1. System: 'inert' electrode|La<sup>2+</sup>, La<sup>3+</sup><sub>(melt)</sub>|"inert" electrode

This section presents the results of a study of the thermoelectric properties of the La(x) + LaCl<sub>3</sub> system (the first class of metal–molten salt systems [43–45]), with a concentration of 0–2.5 mol% lanthanum metal in salt at 1170–1320 K by measuring the initial thermal e.m.f. of the Mo|La(x) + LaCl<sub>3</sub>|Mo thermocell. The measurements were carried out in a cell, whose design and the experimental procedure are described in Ref. [29]. Fig. 5 shows the coefficient of initial thermal e.m.f.,  $\epsilon_{in}$ , and the specific conductivity of this system [46] as a function of the lanthanum metal concentration in lanthanum chloride. The thermoelectric coefficients for mixtures containing more than 2.5 mol% lanthanum metal were omitted since there was a slow and steady variation of thermal e.m.f. at a steady temperature difference  $\Delta T$  in these mixtures; besides, on returning

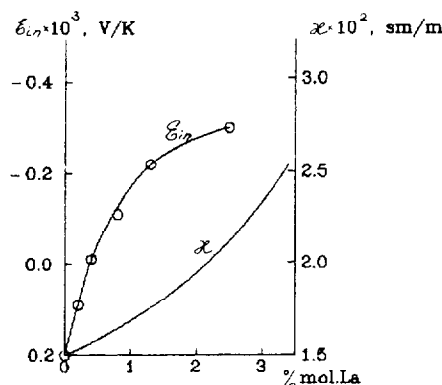


Fig. 5. Coefficient of initial thermal e.m.f.,  $\epsilon_{in}$ , at  $T=1170$ – $1320$  K and electrical conductivity,  $\chi$ , at  $T=1180$  K as a function of lanthanum metal concentration in lanthanum trichloride.

to low  $\Delta T$  values, abnormally high thermal e.m.f. values were observed, which may have been due to thermodiffusion phenomena or adsorption effect on one of the electrodes.

Using an approach reported in Ref. [29], we obtained the following relation for determining the coefficient of initial thermal e.m.f. of the system under consideration:

$$F\epsilon_{in} = -(1-t_e)Q_{ions}^*/T + t_e Q_e^*/T + R \ln \frac{[La^{3+}]}{[La^{2+}]} + \Delta S_{La} \quad (7)$$

where  $t_e$  is the electron transport number,  $Q_{ions}^*$  the heat of identified charge carrier transfer,  $Q_e^*$  the heat of electron transfer and  $\Delta S_{La}$  the so-called ‘excess’ entropy.

The positive  $Q^*$  value indicates that the direction of motion of the diffusing components coincides with the direction of the heat flow. In the thermocell under consideration, the diffusing components of the system (characterized by  $Q_{ions}^*$  and  $Q_e^*$ ) move in the opposite direction to the heat flow (Fig. 6), and hence  $Q^*$  in Eq. (7) will have a negative value.

It follows from the examination of Eq. (7) that when lanthanum is dissolved in  $LaCl_3$ , i.e., when  $t_e$  increases from 0 (pure  $LaCl_3$ ) to approximately 1,  $\epsilon_{in}$  must be first positive ( $F\epsilon_{in} = \Delta S_{La} + Q_{ions}^*/T + \sim$ ) and then decreases and becomes negative since the dominant negative term  $t_e Q_e^*/T$  ( $Q_e^* < 0$ ) increases and the positive terms  $(1-t_e)Q_{ions}^*/T$  and  $R \ln [La^{3+}]/[La^{2+}]$  decrease with increasing metal concentration. This form of the  $\epsilon_{in} = f(x)$  relation, where  $x$  is the lanthanum metal content of molten lanthanum trichloride, is supported by the experiments carried out (see Fig. 5).

As follows from Eq. (7), the thermoelectric coefficient  $\epsilon_{in}$  in pure molten  $LaCl_3$  must be infinitely great. However, this was not observed experimentally, which may be attributed to the presence of some amount of  $La^{2+}$  ions even in pure molten  $LaCl_3$ . The presence of these ions may be caused by the equilibrium:



Thus, Eq. (7) describes qualitatively the experimental data obtained. This allowed us to assume the following scheme of electrode reactions that may proceed on the ‘hot’ and ‘cold’ thermocell electrodes:



Heat is transferred from the ‘hot’ to the ‘cold’ electrode, and mass is transferred in the opposite direction (see Fig. 6).

### 2.3.1.2. System: ‘inert’ electrode| $La^{2+}$ , $La^{3+}$ in the molten eutectic $LiCl-KCl$ mixture|‘inert’ electrode

From the standpoint of studying heat transfer and electrotransfer processes in the  $La(x) + LaCl_3$  system, the effect of the medium is of a certain interest.

Lanthanum is known to displace sodium and potassium from molten  $NaCl$  and  $KCl$ . The reaction  $La + 3RCl = LaCl_3 + 3/2R_2$  results in a rapid increase in the concentration of lanthanum trichloride in the electrolyte, especially when the alkali metal sublimates from the salt melt. This makes it actually impossible to measure reliably thermal e.m.f. as a function of lanthanum ion concentration in molten chlorides, not only as a function of the above alkali metals but also of that of other alkali metals at a high temperature. At the same time, Smirnov [47] showed that lanthanum does not interact noticeably with the molten eutectic  $LiCl-KCl$  mixture at relatively low temperatures (693–963 K). Besides, the  $LiCl-KCl$  melt has the lowest thermal conductivity, a high electrical conductivity and a broad operating temperature range (650–1730 K), which distinguishes it from the other chlorides as a promising solvent for DTEC devices.

The coefficients of initial thermal e.m.f.,  $\epsilon_{in}$ , of the thermogalvanic cell: glassy carbon| $La(x) + LaCl_3$  in the eutectic  $LiCl-KCl$  mixture|glassy carbon were measured for different lanthanum metal ( $x$ ) contents of the  $La(x) + LaCl_3$  mixture and  $La(x) + LaCl_3$  mixture contents of the supporting electrolyte.

The  $LaCl_3 + La(x)$  system was fused in crucibles made of special ceramic, which was inert to the medium under study, for 4 h at 1230 K [45]. To prepare a eutectic mixture (59 mol%  $LiCl$ ), chemically pure anhydrous  $LiCl$  and  $KCl$  were used. The eutectic mixture was prepared by a method similar to that reported in Ref. [48]. Corrosion tests allowed us to use glassy carbon rods as the electrode material. Thermal e.m.f. measurements and data processing to determine the coefficient of initial thermal e.m.f. were carried out as in Ref. [29]. The coefficient of initial thermal e.m.f.,  $\epsilon_{in}$ , remained constant over the temperature range from 750 to 870 K for all compositions studied.

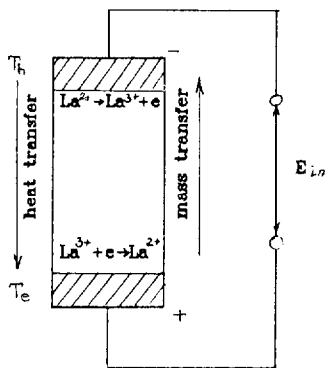


Fig. 6. Scheme of transfer processes in a thermoelectric cell with the molten  $La(x) + LaCl_3$  mixture.



One of the resulting plots of the coefficient of initial thermal e.m.f.,  $\epsilon_{in}$ , against the concentration of the La(0.2 mol%) + LaCl<sub>3</sub> mixture in the LiCl–KCl melt is shown in Fig. 7. All the other plots (for higher La concentrations in LaCl<sub>3</sub>) were similar in shape.

To examine the plots of  $\epsilon_{in}$  against the La(x) + LaCl<sub>3</sub> content of LiCl–KCl obtained, certain assumptions are necessary as to the nature of charge carriers in the system under investigation. Smirnov [47] showed that dilute lanthanum trichloride–alkali chloride mixtures should be regarded as solutions of complex compounds of the Me<sub>3</sub>LaCl<sub>3</sub> type and not LaCl<sub>3</sub> in an excess of MeCl (Me = alkali metal). Solutions of metal Me<sub>3</sub>LaCl<sub>6</sub> in MeCl must be close to the ideal solutions in behaviour since, when they are further diluted with alkali chlorides, there are no considerable changes in bonds between ions. It is reasonable, in our opinion, to assume that divalent lanthanum ions are present in complex form in the melt. It follows that the system under consideration is not an ionic–electronic liquid by contrast to La(x) + LaCl<sub>3</sub> and it is close to the Cd(x) + CdI<sub>2</sub> system in its properties as an ideal ionic melt. Therefore, an equation, like Eq. (5), for the coefficient of initial thermal e.m.f. [3] describes qualitatively the concentration dependence of  $\epsilon_{in}$  presented in Fig. 7. It should be also noted that all concentration dependences of  $\epsilon_{in}$  in the semilogarithmic coordinates are linear.

The afore-said allows one to assume the following scheme of electrode reactions that may take place on the ‘hot’ and ‘cold’ electrodes of a thermocell: LaCl<sub>6</sub><sup>3-</sup> → LaCl<sub>4</sub><sup>2-</sup> + e<sup>-</sup> on the ‘hot’ electrode and LaCl<sub>2</sub><sup>2-</sup> + e<sup>-</sup> → LaCl<sub>3</sub><sup>3-</sup> on the ‘cold’ electrode. Thus, the overall reaction in the electrochemical DTEC system studied consists in the diffusive transfer of complex lanthanum ions in the lowest oxidation state and heat transfer in the same direction – from the ‘hot’ electrode to the ‘cold’ one.

The expedience of using an electrochemical system such as LTM in thermoelectric converters was assessed by means of the efficiency factor or quality of the thermoelectric material, Z. Using Eq. (2), we obtain:

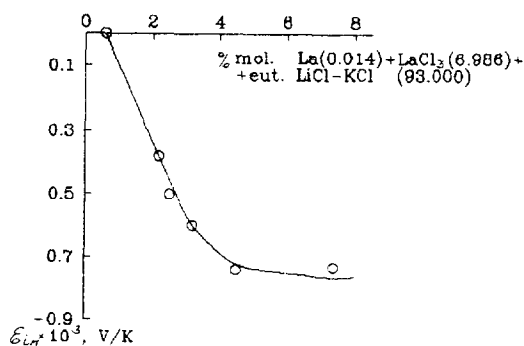


Fig. 7. Coefficient of initial thermal e.m.f.,  $\epsilon_{in}$ , as a function of the La(0.2 mol%) + LaCl<sub>3</sub> mixture concentration in the eutectic LiCl–KCl melt.  $T = 720\text{--}870$  K.

$$Z = \sim 0.5 \times 10^{-3} \text{ K}^{-1}.$$

The electrochemical system considered is superior to DTEC systems with aqueous and nonaqueous organic electrolytes in energy characteristics and can be used as a liquid heat carrier in thermoelectric converters with a nuclear or radioisotope heat source over a broad operating temperature range and in heat flow sensors.

### 2.3.1.3. System: ‘inert’ electrode|Cd<sub>2</sub><sup>2+</sup>, Cd<sub>(melt)</sub><sup>2+</sup>||‘inert’ electrode

The Cd(x) + CdI<sub>2</sub> melt was chosen as a representative of the second class of metal–molten salt systems. This melt is close to perfect ionic melts in nature, which allowed us to interpret the data obtained in terms of known concepts of this type of electrochemical systems and the relations obtained by us.

The results of the study of the system in a non-isothermal field and their interpretation are presented in Ref. [3]. Therefore, we confine ourselves to the experimental results that are necessary for estimating the thermoelectric conversion capacity.

The coefficients of initial thermal e.m.f.,  $\epsilon_{in}$ , for the compositions studied were calculated by the least-squares method from initial thermal e.m.f. – ‘hot’ electrode temperature relations, and are shown in Fig. 8. The maximum  $\epsilon_{in}$  value is  $1.65 \times 10^{-3}$  V/K, and the minimum value is  $0.3 \times 10^{-3}$  V/K.

Voltammetric curves for the thermocell based on the system under investigation were examined for seven compositions, which differed in cadmium metal content; it was 0.2, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 mol% respectively. A typical voltammetric curve is shown in Fig. 9, the other characteristics are given in Tables 1 and 5.

It follows from the data obtained that the electrochemical system under consideration has high Z-factor ( $\sim 1 \times 10^{-3} \text{ K}^{-1}$ ) and power factor ( $5 \times 10^{-4} \text{ W}/(\text{mK}^2)$ ) values. LTM based on the system studied can find application in devices where liquid materials act both as heat carrier and as thermoelectric material.

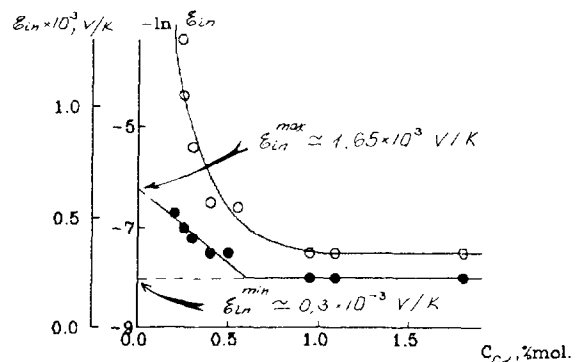


Fig. 8. Coefficient of initial thermal e.m.f., (●)  $\epsilon_{in}$ , and (○)  $\ln \epsilon_{in}$  as a function of cadmium metal concentration,  $C_{Cd}$ , in cadmium iodide for the electrochemical system Mo|Cd(x) + CdI<sub>2(melt)</sub>|Mo.  $x = 0\text{--}5$  mol%,  $T = 720\text{--}780$  K.

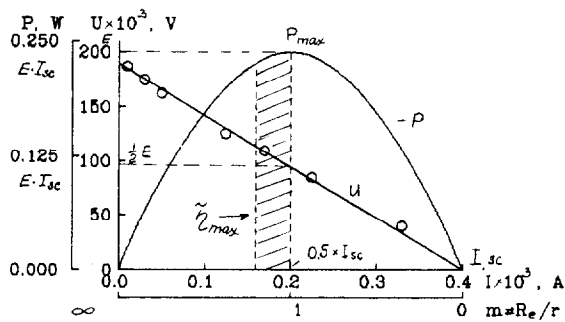


Fig. 9. Voltammogram of the thermocell Mo|CdI<sub>2</sub> + Cd(0.5 mol%)|Mo. The maximum power in the load circuit is observed when the load resistance,  $R_e$ , and the internal resistance,  $r$ , of the thermocell are equal, i.e., at  $m = 1$ .

Table 5

Discharge characteristics of a thermocell mock-up based on the Mo|Cd<sub>2</sub><sup>2+</sup>, Cd<sub>(melt)</sub><sup>+</sup>|Mo system;  $\Delta T = 800 - 700 = 100$  K

Component content (mol.%)		E.m.f. $E \times 10^3$ (V)	Short-circuit current $I_{sc} \times 10^9$ (A)	Power $P \times 10^6$ (W)
Cd	CdI <sub>2</sub>			
0.2	99.8	159	0.142	22.4
0.5	99.5	185	0.400	74.0
1.0	99.0	150	0.306	45.8
2.0	98.0	166	0.292	48.4
3.0	97.0	134	0.343	45.9
4.0	96.0	169	0.285	48.2
5.0	95.0	145	0.332	48.1

### 2.3.2. Systems with semiconductor electrodes

Another nonconventional electrochemical system studied, which can be hardly classified among known thermogalvanic cells, is the system semiconductor/salt melt containing ions of metal being part of the semiconductor electrode.

There is no information found in the literature concerning the study of the thermoelectric properties of electrochemical systems based on molten electrolytes and semiconductor electrodes, though the thermoelectric properties of semiconducting materials have been fairly well studied (Table 1) [14,15,48–52]. Such investigations are of interest not only for developing concepts of electrode processes occurring at the semiconductor/melt interface in a nonisothermal field but also for search for basically new thermoelectric conversion systems and improving the currently used ones.

The investigations were carried out in low-temperature melts of the following compositions (mol%): AlCl<sub>3</sub>(66) + NaCl(20) and KCl(14) + BiCl<sub>3</sub>( $x$ ) over a temperature range from 403 to 623 K. Rods made of semiconducting materials (p-type: 74 mol% Sb<sub>2</sub>Te<sub>3</sub> and 26 mol% Bi<sub>2</sub>Se<sub>3</sub>; n-type: 80 mol% Bi<sub>2</sub>Te<sub>3</sub> and 20 mol% Bi<sub>2</sub>Se<sub>3</sub>) with  $\epsilon \cdot 10^9 = (0.18 - 0.22)$  V/K were used as working electrodes. A melt containing mainly aluminates, which

are formed by fusing together starting salts according to the reaction:  $2\text{AlCl}_3 + \text{NaCl} + \text{KCl} \rightarrow \text{NaAlCl}_4 + \text{KAlCl}_4$ , was used as the supporting electrolyte to provide a low-temperature molten medium. Addition of definite amounts of bismuth trichloride to the electrolyte provided appropriate concentrations of potential-determining bismuth ions.

For the system studied, dependences of the initial thermal e.m.f.  $\epsilon_{in}$ , on 'hot' electrode temperature variation were obtained using the above-mentioned semiconducting materials as electrodes. By processing these data, we determined temperature dependences of thermoelectric coefficients for thermocells with different bismuth trichloride contents of the supporting electrolyte (Fig. 10) and those for thermocells with different semiconductor electrode combinations.

As follows from the analysis of experimental data, the plots of the coefficient of initial thermal e.m.f. against temperature for semiconductor electrode/molten electrolyte systems are nonlinear, and each of them can be divided into two regions. The first region (between 400 and 500 K) exhibits pronounced thermoelectric coefficient maxima (for a combination of p-p type electrodes  $\epsilon_{max} = 1.66 \times 10^{-3}$  V/K, for that of n-n type electrodes  $\epsilon_{max} = 2.12 \times 10^{-3}$  V/K and for that of n-p type electrodes  $\epsilon_{max} = 2.25 \times 10^{-3}$  V/K at  $T = 460$  K<sup>1</sup>). The highest absolute  $\epsilon_{in}$  value for a thermocell with n-p type electrodes as against other thermocell types may be accounted for by the combining of the thermoelectric effect of a semiconducting pair of an n-type and a p-type electrode with that of the electrochemical system: semiconductor electrode/molten electrolyte with potential-determining bismuth ions.

When the temperature is further increased (the second temperature region,  $T = 500 - 600$  K), the thermoelectric coefficient values remain actually unchanged

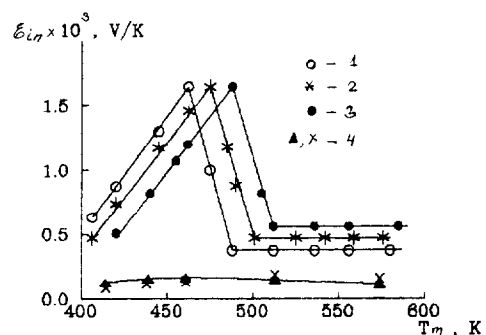


Fig. 10. Temperature dependence of the thermoelectric coefficient  $\epsilon_{in}$  of the electrochemical system p-type semiconductor[BiCl<sub>3</sub>( $x$ ) in AlCl<sub>3</sub>(66 mol%) + NaCl (20 mol%) + KCl(14 mol%)]p-type semiconductor: (1)  $x = 2.0$  mol%; (2)  $x = 3.0$  mol%; (3)  $x = 5.8$  mol%, and (4) of p-type semiconductor.

<sup>1</sup> The maximum Z-factor value for a thermocell based on the PbTe + 0.5% Pb + 0.2% Bi semiconductor is also observed at  $T = 460$  K [53].

for the same thermocell. The  $\epsilon_{in}$  value of approximately  $0.45 \times 10^{-3}$  V/K for this temperature region is twice as higher as the  $\epsilon$  value for a purely semiconducting material ( $\epsilon = 0.18 \times 10^{-3} - 0.22 \times 10^{-3}$  V/K, curve 4, Fig. 10).

Thus, the thermoelectric properties of the type of electrochemical systems considered differ from those of the systems studied before with reversible and 'inert' electrodes and both aqueous and molten electrolytes, for which the thermoelectric coefficient is, in most cases, independent of the temperature, not only in the thermoelectric coefficient value but also in the nature of temperature dependence.

### 3. Conclusions

The main parameters (operating temperature range, efficiency, efficiency factor, power factor) of the electrochemical systems discussed in the present paper are given in Table 1, together with the estimation of similar parameters for known classes of thermoelectric materials (metals, semiconductors and electrolyte materials: aqueous and nonaqueous organic electrolytes, salt melts). By analogy with solid thermoelectric materials, LTMs can be divided into the following three groups, depending on the operating temperature range: low-temperature materials (up to 600 K), medium-temperature materials (up to 900 K), and high-temperature materials (over 900 K). As follows from Table 1, galvanic thermoelectric materials can be used over the whole, practically expedient temperature range: aqueous and organic aprotic materials in the low-temperature region and salt melts in the medium- and high-temperature regions.

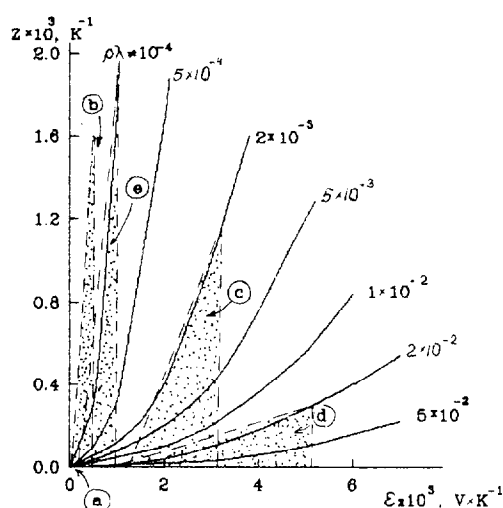


Fig. 11. Comparative characterization of the thermoelectric conversion ability of various classes of thermoelectric materials: (a) metals; (b) semiconducting materials, and electrolyte materials: (c) aqueous solutions, (d) organic solutions, (e) melts.

Thus, the DTEC processes have been effected in a broad temperature range using nonconventional electrochemical redox systems based on aqueous and non-aqueous electrolytes.

The data given in Table 1 and in Fig. 11 support the possibility of using the electrochemical systems studied in DTEC devices: the thermoelectric coefficient and Z-factor are comparable with or higher than those of the electronic and semiconducting materials of modern thermoelectric conversion systems.

### 4. List of symbols

$a_i$	activities of the electrolyte components ( $\text{mol l}^{-1}$ )
$E$	electromotive force (e.m.f.) (V)
$C$	concentration
$F$	Faraday constant ( $96\,500 \text{ C mol}^{-1}$ )
$h$	number of electrons of the ion with the highest valency
$I$	current (A)
$I_{sc}$	short-circuit current (A)
$l$	number of electrons of the ion with the lowest valency
$M$	index of efficiency
$P$	power (W)
$Q_{ions}^*$	heat of transfer of identified current-carriers ( $\text{J mol}^{-1}$ )
$R$	universal gas constant ( $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ )
$R_H$	resistance of load ( $\Omega$ )
$r$	internal resistance ( $\Omega$ )
$\Delta S$	excess entropy ( $\text{J K}^{-1} \text{ mol}^{-1}$ )
$T_0$	temperature under initial conditions (K)
$T_c$	temperature of 'cold' electrode (K)
$T_h$	temperature of 'hot' electrode (K)
$t_k$	transport number of ion
$t_e$	transport number of electron
$Z$	figure-of-merit of Z-factor ( $\text{K}^{-1}$ )

### Greek letters

$\epsilon$	coefficient of thermo-e.m.f. (V/K)
$\epsilon_{in}$	coefficient of initial thermo-e.m.f. ( $\epsilon$ under initial conditions) (V/K)
$\epsilon_{in}^0$	value $\epsilon_{in}$ independent of the electrolyte composition and characteristic of the given electrode (V/K)
$\eta_{max}$	maximum efficiency (%)
$\chi$	conductivity ( $\Omega^{-1} \text{ m}^{-1}$ )
$\lambda_A$	heat conductivity of electrode material ( $\text{W m}^{-1} \text{ K}^{-1}$ )
$\lambda_B$	heat conductivity of electrolyte ( $\text{W m}^{-1} \text{ K}^{-1}$ )
$\rho_A$	resistivity of electrode material ( $\Omega \text{ m}$ )
$\rho_B$	resistivity of electrolyte ( $\Omega \text{ m}$ )
$\Pi_i$	product sign

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