# Use of simple ac technique to determine the ionic and electronic conductivities in pure and Fe-substituted SrSnO$_3$ perovskites

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## Abstract

We report the use of a new method to separate the ionic and electronic contributions to the conduction of solids that involves the use and proper interpretation of low amplitude variable frequency ac measurements. This is a relatively simple technique and has some advantages over the dc methods that are normally employed for this purpose, the Tubandt Faraday's Law method, the dc assymetric polarization technique that is often called the Hebb–Wagner method, and the dc open circuit potential method. The temperature dependence of the transference numbers of several members of the SrSnO$_3$ family of perovskite-like oxides, both with and without Fe substitution for some of the Sn, determined by this new method are reported. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Electrical charge can be transported within solids by the net macroscopic motion of either electronic or ionic species. In materials that are of interest for use as solid electrolytes it is important that the charge transport is predominantly related to ionic motion. Minority electronic conduction is generally considered to be deleterious. On the other hand, ionic charge transport is generally not desired in materials such as electronic semiconductors, for it can cause changes in the properties of junctions as well as influence the concentration of traps and other features of the micro-structure. Between these two extremes are a number of materials that are mixed ionic and electronic conductors. Such mixed-conductors play important roles in a number of different technologies, being employed as oxidation and hydrogenation catalysts, as chemical separation membranes, reactants or mixed-conducting matrices in the micro-structure of battery electrodes, and as fuel cell electrodes.

A number of methods have been developed to evaluate the separate electronic and ionic components of the total charge transport. These include the Tubandt dc method [1] that compares the amount of mass transferred by the passage of electrical charge with that expected from the Faraday equation, the dc assymetric polarization method that is sometimes called the Hebb–Wagner method [2], and the comparison of the open circuit voltage of galvanic cells with the expected thermodynamic value [3,4].

Another method involves the employment and proper interpretation of low amplitude variable frequency ac measurements, an experimental procedure that is often called impedance spectroscopy and employed for other purposes, such as the evaluation of the ionic conductivity of solid electrolytes.

## 2. Transference numbers of individual species

If more than one species can carry charge in a solid or liquid, it is often of interest to know the relative conductivities or inversely, the impedances of different species. The parameter that is used to describe the contributions of individual species to the transport of charge is the transference number, sometimes called the Hittorf transference number [5]. This is defined as the fraction of the total electrical current that is carried by a particular species when an electrical potential difference is imposed upon the adjacent electrodes.

In the simple case that electrons and one type of ions can move through such an electrochemical cell, we can define

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the transference number of ions as $t_i$ and electrons as $t_e$, where

$$t_i = \frac{i_i}{(i_i + i_e)} \qquad (1)$$

and

$$t_e = \frac{i_e}{(i_i + i_e)} \qquad (2)$$

and $i_i$ and $i_e$ are their respective partial currents. We can readily see that the sum of the transference numbers of all mobile charge-carrying species is unity. In this case we have

$$t_i + t_e = 1 \qquad (3)$$

Instead of expressing transference numbers in terms of currents, we can also write them in terms of the related impedances, $Z_i$ and $Z_e$. For the case of a material containing these two mobile species, and the transport of charge by the motion of the ions under the influence of an applied voltage $E_{appl}$,

$$t_i = \frac{E_{appl}/Z_i}{(E_{appl}/Z_i + E_{appl}/Z_e)} = \frac{Z_e}{Z_i + Z_e} \qquad (4)$$

and likewise for electrons

$$t_e = \frac{Z_i}{Z_i + Z_e} \qquad (5)$$

Whereas these parameters are often thought of as properties of the electrolyte or mixed-conductor, in actual experiments they can also be influenced by what happens at the interfaces between the electrolyte or mixed-conductor and the electrodes. They are only properties of the electrolyte or mixed-conductor alone if there is no impedance to the transfer of either ions or electrons across the electrolyte/electrode interface or mixed-conductor/electrode interface, or within the electrodes.

The transference number is also not a constant for a given material, but instead, is dependent upon the chemical potentials of the constituent components within it. Thus, it is dependent upon the local composition and will not be uniform throughout an electrolyte in a galvanic cell in which the electrodes have different values of the chemical potentials.

## 3. Variable frequency small signal ac method

Variable frequency ac methods are now often used to evaluate the charge transport properties of potential solid electrolytes. They involve the use of electronically-conducting electrodes on two sides of the solid to be investigated. The experimental arrangement generally involves putting a thin slab of the material to be investigated between a pair of electronically-conducting, but ionically-blocking electrodes.

Both theoretical and experimental considerations have shown that such an interface between a solid electrolyte, considered to be a purely ionic and a purely electronic conductor can be simply modeled as a parallel plate capacitor [6]. The excess ionic charge on one side of the ionically-blocking interface is balanced by excess electronic charge in the adjacent metal electrode.

It is often useful to interpret physical processes by the use of equivalent electrical circuits. This is not always straightforward, however, for more than one equivalent circuit can often be devised that will mimic the experimental results. It is most useful to use a circuit that most directly reflects the physical arrangement and processes in the experiment. For instance, parallel networks would obviously not be appropriate for two physical processes that are known to occur in sequence or in series. Also, a series configuration would not be appropriate for physical processes that are known to occur in parallel.

Since the experiment that is being discussed here involves the transport of electrical charge from one electrolyte/electrode interface to the other by passing through the electrolyte, which has a finite resistance, $R_i$, this physical configuration can be represented by a simple electrical equivalent circuit shown in Fig. 1 at low frequencies. The capacitive properties of the two electrolyte/electrode interfaces are combined into a single capacitance, $C_{int}$.

At higher frequencies, however, the experimental configuration begins to exhibit an additional geometrical capacitance due to the presence of a material (the sample being studied) with a finite dielectric constant between the two parallel metallic electrodes. This capacitance, $C_{geom}$, acts across the whole configuration, and typically has very small values. Thus, the equivalent circuit becomes that shown in Fig. 2, which is often called the "Debye circuit".

This equivalent circuit has the desirable characteristic that it also corresponds closely to the physical arrangement. Typical values of $C_{geom}$ and $C_{int}$ are $10^{-12}$ and $10^{-6}$ F/cm$^2$, respectively.

The experimental results are typically expressed in terms of a plot of the imaginary and real parts of the impedance, or the imaginary and real parts of the admittance, against each other on the complex plane.

Assuming that there is no significant electronic conductivity in the solid electrolyte phase and that the ionic species are completely blocked at the electrolyte/electrode interfaces, the corresponding complex plane plot is shown schematically in Fig. 3. If the temperature is varied, the time



Fig. 1. Simple equivalent circuit for an electrochemical cell with an ionic conductor between two ionically-blocking, but electronically-conducting, electrodes.
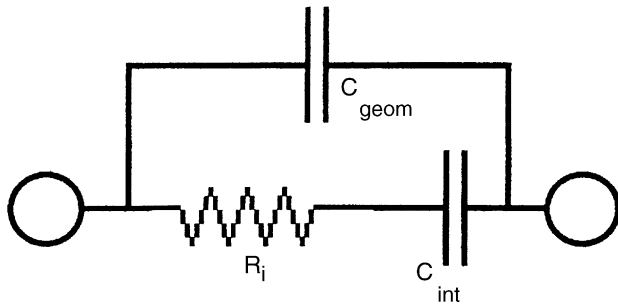
Fig. 2. Debye equivalent circuit corresponding to the physical configuration of a solid electrolyte between two ionically-blocking, but electronically-conducting electrodes.

constants of the various processes change and the experimentally observable portion of the total frequency response (the frequency window) shifts.

These results deviate from the behavior of the ideal Debye equivalent circuit in that the low frequency tail is not truly vertical, but instead is a straight line inclined at a finite angle from the vertical.

It has been shown that this deviation from ideal Debye circuit behavior relates to processes that occur at the solid electrolyte/electrode interface [7], and that the electrical response in that range of frequency can be represented by an impedance of the form

$$1Z = A\omega^{-\alpha} - jB\omega^{-\alpha} \tag{6}$$

that acts in series with the bulk ionic impedance. However, this is a detail that is not important to the results presented here.

If the electroactive species is not blocked at the interface, but diffuses into or out of one or both of the electrodes as a neutral reaction product according to Fick's Second Law the low frequency data will fall onto a straight line with a slope of 45°, so the value of $\alpha$ in that case will be 1/2 if the interface is planar. This involves the introduction of a so-called Warburg admittance or impedance into the equivalent circuit. This has been treated fully elsewhere [8], and since it is not directly related to the subject of this paper, it will also not be considered here.
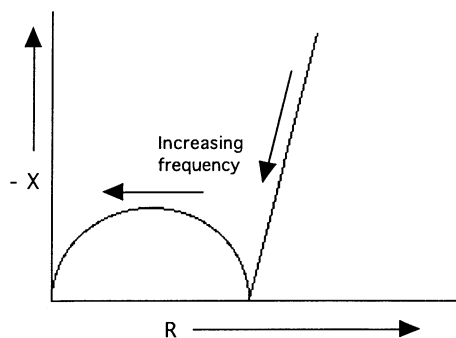


Fig. 3. Schematic drawing of the type of complex plane plot that is often observed for the experimental arrangement that should correspond to the Debye equivalent circuit.
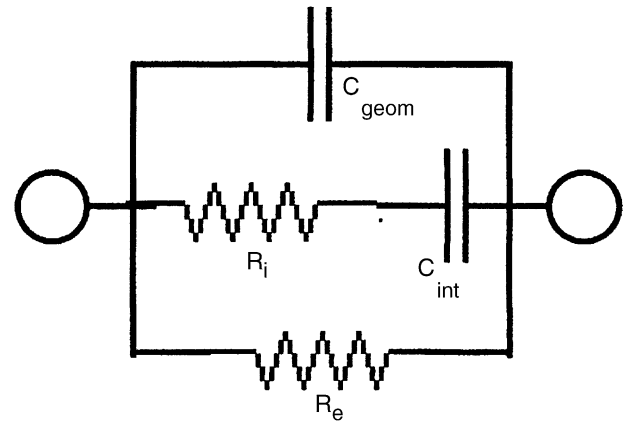


Fig. 4. Equivalent circuit for an experimental system in which both electronic current and ionic current can flow through the electrolyte. Since the interface does not block the flow of electronic current, $R_e$ shunts both $R_i$ and $C_{int}$.

## 4. Influence of electronic leakage through the ionic conductor

If the material between the electrodes is a mixed-conductor, with both ionic and electronic contributions to charge transfer, the equivalent circuit must be modified to include an electronic current path in parallel with the ionic current path. This is shown in Fig. 4.

If the electronic resistance is much lower than the ionic resistance, all of the other components of the equivalent circuit are shorted out, and there is only a single point at the low frequency end of the figure in the complex impedance plane.

## 5. Case in which both ionic and electronic transport are significant

If there is a substantial amount of ionic transport, as well as an electronic shunt at low frequencies, the complex plane plot will look like as shown in Fig. 5. There are two semicircles, representing the parallel combination of the electronic resistance and the geometrical capacitance at low frequencies, and the parallel combination of the ionic resistance and the geometrical capacitance at the higher frequencies. There is no low frequency tail, as the interfacial capacitance is shunted by the electronic current at low frequencies, as discussed above.

There are two intercepts on the resistance axis, designated as $R_1$ and $R_2$. The one at low frequencies, $R_2$, is the same as the dc value, and thus is merely the electronic resistance, $R_e$. At higher frequencies the impedance due to the relatively large interfacial capacitance becomes insignificant and is not observed in the measurements. The equivalent circuit of Fig. 4 then becomes a parallel arrangement with three legs, the geometric capacitance and the two resistances, which are in a parallel configuration. This leads to the second semicircle in the impedance plane. The resulting intercept on the
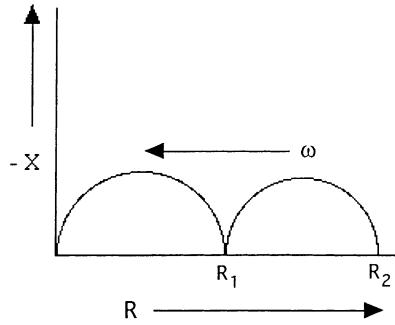
Fig. 5. Complex impedance plane plot for the case that both ionic and electronic transport are significant.

resistance axis at the higher frequency, $R_1$, is a combination of the two parallel resistances, $R_i$ and $R_e$. Thus,

$$\frac{1}{R_1} = \frac{1}{R_i} + \frac{1}{R_e} \tag{7}$$

which can be rewritten to give

$$R_1 = \frac{R_e R_i}{R_e + R_i} \tag{8}$$

The ionic and electronic fractions of the total conductance, and thus of the conductivity, can be found.

The ionic conductance $G_i$ is

$$G_i = \frac{1}{R_i} = \frac{1}{R_1} - \frac{1}{R_e} = \frac{R_2 - R_1}{R_1 R_2} \tag{9}$$

and the electronic conductance $G_e$ is

$$G_e = \frac{1}{R_e} = \frac{1}{R_2} \tag{10}$$

The total conductance $G_{total}$ is

$$G_{total} = G_i + G_e = \left(\frac{R_2 - R_1}{R_1 R_2}\right) + \frac{1}{R_2} = \frac{1}{R_1} \tag{11}$$

The transference numbers of the ionic and electronic species are equal to their respective partial conductances

$$t_i = \frac{G_i}{G_{total}} = \frac{R_2 - R_1}{R_2} \tag{12}$$

and

$$t_e = \frac{G_e}{G_{total}} = \frac{R_1}{R_2} \tag{13}$$

Thus, it can be seen that the transference numbers of the ionic and electronic species can be obtained by simple evaluation of the relative values of the two intercepts on the real axis in a complex impedance plane plot.

If the ionic transference number is relatively large, and the electronic transference number is relatively small, as is desired for useful electrolytes, the right hand, lower frequency semicircle is considerably larger than the higher frequency semicircle. In the extreme case of very little electronic conduction, $R_1$ approaches zero. On the other

hand, if the electronic conduction is dominant, the low frequency semicircle becomes quite small, and $R_1$ approaches $R_2$. There is no low frequency capacitive tail on the complex impedance plot in either case.

The relationships between the values of the intercepts of the data with the real impedance axis and the specific resistances within the sample for several cases are given in Tables 1 and 2.

## 6. Experimental aspects

SrSn$_{1-x}$Fe$_x$O$_{3-\delta}$ perovskite oxides with a range of values of $x$ (0–1) were prepared by solid-state reaction of stoichiometric mixtures of SrCO$_3$ (> 99.9%, Aldrich), SnO$_2$ (99.9%, Alfa) and Fe(CO$_2$)$_2$·2H$_2$O (99%, Aldrich) at 1000 °C for 24 h and 1300 °C for 24 h with intermittent grinding and pelletizing using isostatic pressure. The sintered pellets were cut into small coin-shaped cylinders with a thickness of 2–6 mm and diameter about 10 mm. A portion was also ground to fine powder for X-ray diffraction
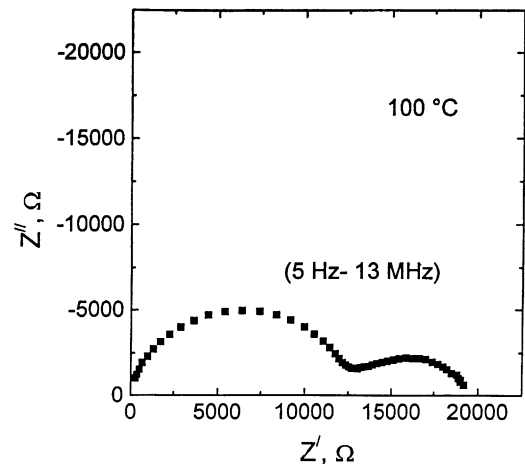
Table 1
Interpretation of the intercepts on the real axis

| Type of conduction | $R_1$ | $R_2$ |
|---|---|---|
| Ionic conduction only | $R_i$ | |
| Electronic conduction only | $R_e$ | |
| Ionic with electronic shunt | $(R_e R_i)/(R_e + R_i)$ | $R_e$ |

Table 2
Transference numbers

| Type of conduction | Ionic transference number | Electronic transference number |
|---|---|---|
| Ionic conduction only | 1.0 | 0.0 |
| Electronic conduction only | 0.0 | 1.0 |
| Ionic with electronic shunt | $(R_2 - R_1)/R_2$ | $R_1/R_2$ |



Fig. 6. Complex impedance plane plot for SrSn$_{0.8}$Fe$_{0.2}$O$_3$ in air at 100 °C.

evaluation using a Siemens D-5000 powder diffractometer with Cu Kα radiation at room temperature.

Electrical conductivity measurements were made in air over the temperature range 25–800 °C using platinum paste electrodes heated to 850 °C for 1 h using an HP 4192 A impedance analyzer over the frequency range 5 Hz– 13 MHz. The powder X-ray data indicated the presence of a perovskite-like structure in all cases. Details of the structure, electrical conductivity and physical characterization results will be presented elsewhere [9].

An example of the results of the ac measurements in shown in Fig. 6.

## 7. Evaluation of the transference numbers

Experimental results on the use of the variable frequency ac method to study the properties of materials in the $PrO_x$ family, which have structures related to fluorite, were recently reported [10,11]. It was shown that this material is a mixed ionic–electronic conductor over a wide range of conditions [12]. Using the complex impedance figures given in that paper [10], the ionic and electronic transference numbers, and their variation with temperature, could be evaluated by the use of the methods and interpretation presented here [13,14].

Tables 3 and 4 show the compositions and the values of $R_i$ and $R_e$ that were obtained, as well as the ionic and electronic transference numbers, for members of the $SrSn_{1-x}Fe_xO_{3-\delta}$ family.

The temperature dependencies of the ionic and electronic transference numbers of these materials are shown in Figs. 7 and 8. The relative increase of the electronic transference numbers with increasing temperature is consistent with the expectation that the electronic conductivity would have a larger activation energy than that of the ionic conductivity in such materials.

Table 3
Identification of materials studied

| Designation | Material | $x$-Value |
|---|---|---|
| A | $SrSnO_3$ | |
| B | $SrSn_{1-x}Fe_xO_{3-\delta}$ | 0.1 |
| C | $SrSn_{1-x}Fe_xO_{3-\delta}$ | 0.2 |
| D | $SrSn_{1-x}Fe_xO_{3-\delta}$ | 0.4 |

Table 4
Resistances and transference numbers observed

| Material | Temperature (°C) | $R_1$ | $R_2$ | $R_i$ | $R_e$ | $t_i$ | $t_e$ |
|---|---|---|---|---|---|---|---|
| A | 200 | 30000 | 65000 | 55714 | 65000 | 0.54 | 0.46 |
| A | 250 | 11500 | 20000 | 27059 | 20000 | 0.42 | 0.58 |
| A | 295 | 5000 | 8500 | 12143 | 8500 | 0.41 | 0.59 |
| A | 340 | 2000 | 3000 | 6000 | 3000 | 0.33 | 0.67 |
| B | 200 | 30000 | 65000 | 55714 | 65000 | 0.54 | 0.46 |
| B | 250 | 11000 | 20000 | 24444 | 20000 | 0.45 | 0.55 |
| B | 295 | 5000 | 8500 | 12143 | 8500 | 0.41 | 0.59 |
| B | 350 | 2000 | 3000 | 6000 | 3000 | 0.33 | 0.67 |
| C | 100 | 12500 | 19000 | 36538 | 19000 | 0.34 | 0.66 |
| C | 143 | 3000 | 3900 | 13000 | 3900 | 0.23 | 0.77 |
| C | 191 | 850 | 950 | 8075 | 950 | 0.11 | 0.89 |
| D | 25 | 6000 | 8500 | 29400 | 8500 | 0.29 | 0.71 |
| D | 62 | 1200 | 1450 | 6960 | 1450 | 0.17 | 0.83 |

## 8. Summary

A new and relatively simple method based on impedance spectroscopy using ionically-blocking electrodes has been presented that can be useful in interpreting experimental data on mixed-conductors when there is not a large difference between the ionic and electronic impedances. It does not require high ionic conductivity and does not involve passing a significant amount of material through the sample.
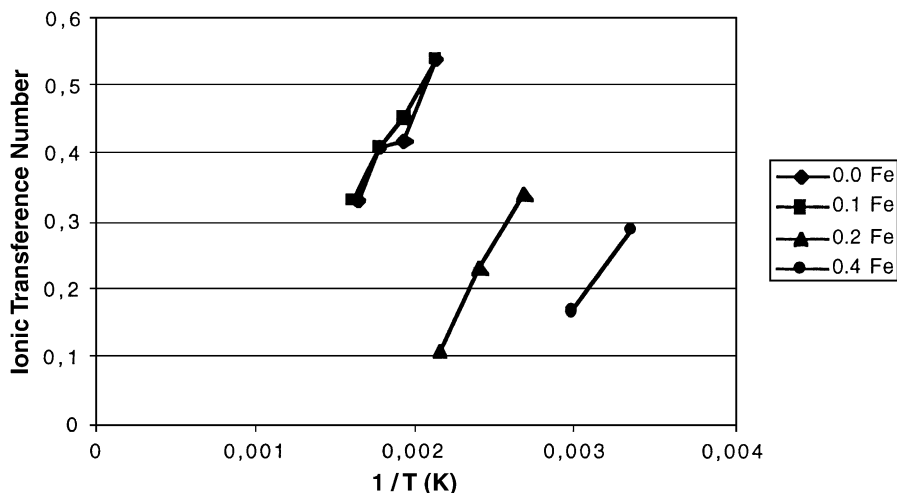


Fig. 7. Temperature dependence of the ionic transference number of $SrSn_{1-x}Fe_xO_3$.

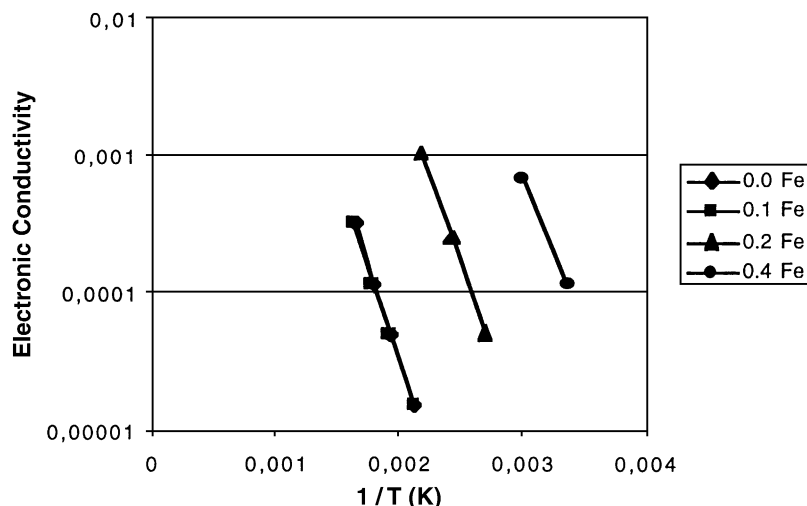Fig. 8. Temperature dependence of the electronic conductivity of $SrSn_{1-x}Fe_xO_3$.

Also, it does not require the imposition of different thermo-dynamic conditions upon the two sides of the sample and waiting for slow equilibration of species within it. The whole sample can be surrounded by the same atmosphere, so data can be obtained as a function of the thermodynamic environment.

One can easily recognize the presence of a significant amount of electronic leakage through the sample by the absence of a capacitive tail in complex impedance plots at low frequencies. When that is the case, evaluation of the relative values of the intercepts upon the real impedance axis provides information about the ionic and electronic resistances, as well as their respective transference numbers.

When substantial electronic conduction is present, the meanings of these intercept values are distinctly different from when the charge transport is only ionic. This has been shown for the situation in which there is no appreciable impedance due to the presence of transverse internal interfaces, and also for the case in which internal, partially blocking, transverse interfaces are present.

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