

Homework 6 solution

Problem:

Ionic conductivity is an important parameter of performance of a fuel cell electrolyte. Mostly, the performance of a fuel cell, in particular SOFC, is limited due to ionic transport in the electrolyte layer.

There are various methods to measure ionic conductivity of a fuel cell electrolyte. Electrochemical impedance spectroscopy is the most common method to measure the ionic conductivity in a laboratory. The ionic conductivity is generally measured for a range of temperatures of interest and the data is presented in a form of an Arrhenius plot.

Arrhenius equation is given as:

$$\sigma T = \sigma_o \exp\left(\frac{-E_a}{RT}\right)$$

$$\ln(\sigma T) = \ln(\sigma_o) - \frac{E_a}{RT}$$

The activation energy E_a tells about the effect of temperature on a particular ionic transport process in the electrolyte layer, and it can be calculated from the slope of the Arrhenius plot:

$$y = mx + c$$

$$\text{where } y = \ln(\sigma T), \quad x = \frac{1}{T}, \quad m = \frac{-E_a}{R}, \quad \text{and } c = \ln(\sigma_o)$$

For further information, see O'Hayre et al., Fuel cell fundamentals, 2016, Section 4.5.3.

Tables on the next page show experimental temperature dependent conductivity data of two different SOFC electrolyte materials.

- Plot the Arrhenius plot for ionic conductivities for both electrolytes in the same figure. Then calculate the activation energy (in kJ/mol or eV) of the ionic transport process at the lower temperature range (250 °C – 350 °C) and at the higher temperature range (550 °C – 700 °C) based on the data points that show Arrhenius type behavior. (For example in Microsoft Excel, you can use the SLOPE function.)
- Are the activation energies for the lower temperature range and the higher temperature range equal? If not, what does it mean?
- Which of these two electrolytes seems more promising for SOFC applications based on this data?
- Briefly, what other properties a good SOFC electrolyte should have?

Electrolyte 1 (SDC 88 wt-%, Na₂CO₃ + Li₂CO₃ 12 wt-%)

<i>T</i> (°C)	σ_{total} (S/cm)
250	1.06041E-06
300	6.9379E-06
350	3.43447E-05
400	0.000126794
424	0.000252489
438	0.000395115
460	0.000896243
479	0.00278652
489	0.00597731
498	0.025375712
508	0.029001276
550	0.03852258
600	0.051120032
650	0.060321855
700	0.069273267

Electrolyte 2 (SDC 80 wt-%, Na₂CO₃ + Li₂CO₃ + K₂CO₃ 20 wt-%)

<i>T</i> (°C)	σ_{total} (S/cm)
250	5.31E-06
300	8.16E-05
350	0.0008
375	0.0045
380	0.0068
390	0.011
400	0.020
410	0.024
420	0.045
450	0.10
500	0.17
550	0.23
600	0.29
650	0.35
700	0.42

Solution:

a) The Arrhenius plots for ionic conductivities for both electrolytes are presented in the figure below. The numerical calculation tables can be found in the Appendix. The activation energies E_a were determined from the linear parts of the high temperature (HT) and low temperature (LT) regions for both electrolytes, according to the Arrhenius equation

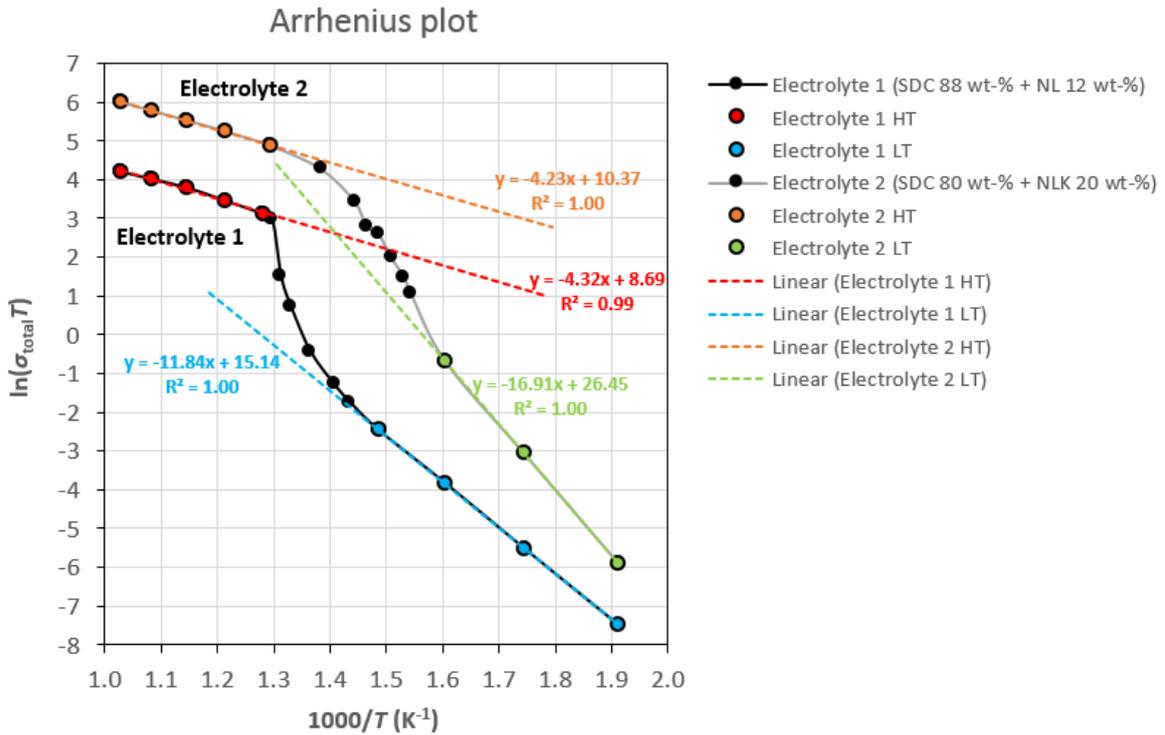
$$\sigma T = \sigma_o \exp\left(\frac{-E_a}{RT}\right)$$

$$\ln(\sigma T) = \ln(\sigma_o) - \frac{E_a}{RT}$$

The dashed lines in the figure are linear fits of the above equation to the data points marked with the corresponding color. More specifically, the fitted line is

$$y = mx + c$$

where $y = \ln(\sigma T)$, $x = \frac{1000}{T}$, $m = \frac{-E_a}{R}$, and $c = \ln(\sigma_o)$



The activation energies E_a (kJ/mol) were calculated from the slope (the unit of m is K) as

$$E_a = -mR$$

where R is the gas constant, $R = 8.314$ kJ/mol/K.

The results are:

Electrolyte 1		Electrolyte 2	
$E_{a,LT}$	$E_{a,HT}$	$E_{a,LT}$	$E_{a,HT}$
98.43 kJ/mol	35.94 kJ/mol	140.62 kJ/mol	35.19 kJ/mol
1.020 eV	0.372 eV	1.457 eV	0.365 eV

(1 eV = 96.49 kJ/mol)

b) We can see from the above results that both electrolytes have markedly different activation energy at the low and high temperature ranges. This means that the ion transport mechanism must be different at the low and high temperature range. In both cases, E_a is higher at the low temperature range than at the high temperature range, which means that the ionic transport process is energetically easier, i.e. less thermal energy from the surrounding is needed for its activation, making the kinetics of the transport faster. More specifically, we learn from Chapter 4 of O’Hayre (2016) that the conductivity of a SOFC electrolyte dominated by extrinsic carriers is (equation 4.61):

$$\sigma = \frac{c(zF)^2 D_0 e^{-\Delta G_{\text{act}}/(RT)}}{RT}$$

where the exponential term comes from the temperature dependence of the diffusion coefficient (equation 4.60)

$$D = D_0 e^{-\Delta G_{\text{act}}/(RT)}$$

Lower activation energy thus means faster increase of conductivity with increasing temperature, but also higher conductivity at a given temperature, if the diffusion coefficient factor D_0 remains the same. In general however, we should expect also D_0 be different if $\Delta G_{\text{act}} = E_a$ is different, because both are related to transport mechanism in question.

But why do we have two different activation energies, and therefore two different transport processes in these electrolyte? The reason is that these electrolytes are composite (mixture) of an SOFC electrolyte material (SDC) and several molten carbonate fuel cell electrolyte material (Na, Li, and K carbonates). The carbonates melt in the temperature medium temperature range providing a step-wise increase in the conductivity due to much better ionic conduction in the molten than in the solid phase. We can see from the Arrhenius plot that the melting (transition) happens at lower temperature for the Electrolyte 2, which is the reason why it reaches higher conductivity sooner, even though at the high temperature range both electrolytes have similar activation energies. It is in these composites really the melting temperature of the carbonate composite part that determines the conductivity at the operating temperatures, and the lowest possible operating temperature, and not so much the activation energy as such.

c) The ultimate performance figure-of-merit for a SOFC electrolyte is the conductivity at the operating temperature of interest, and not the activation energy, as already mentioned. In this case, Electrolyte 2 has higher conductivity at the high temperature range, where SOFCs are used, and is therefore clearly better a better choice with this respect, and therefore more promising electrolyte material for SOFC applications.

d) What do we mean by “promising”? Well, conductivity is not the only factor that determined the suitability of a SOFC electrolyte for practical applications. In addition to high conductivity (helped by low activation energy, and in the case of molten carbonates, by low melting temperature), the electrolyte material needs to have most importantly

- low electronic conductivity
- good chemical stability in both reducing and oxidizing environments
- mechanical stability and a matching thermal expansion coefficient with the electrodes
- low gas permeability to avoid gas cross-over, i.e. non-porous and pin-hole-free
- low cost

Appendix: Arrhenius analysis and comparison of two composite SOFC electrolytes

Electrolyte 1: SDC 80 wt% + NLK 20 wt% composite

T (°C)	T (K)	$1000/T$ (K ⁻¹)	σ_{total} (S/cm)	$\ln(\sigma_{\text{total}})$	$\ln(\sigma_{\text{total}} T)$
250	523	1.912	1.06E-06	-13.757	-7.497
300	573	1.745	6.94E-06	-11.879	-5.528
350	623	1.605	3.43E-05	-10.279	-3.845
400	673	1.486	0.000126794	-8.973	-2.461
424	697	1.435	0.000252489	-8.284	-1.737
438	711	1.406	0.000395115	-7.836	-1.270
460	733	1.364	0.000896243	-7.017	-0.420
479	752	1.330	0.00278652	-5.883	0.740
489	762	1.312	0.00597731	-5.120	1.516
498	771	1.297	0.025375712	-3.674	2.974
508	781	1.280	0.029001276	-3.540	3.120
550	823	1.215	0.03852258	-3.257	3.456
600	873	1.145	0.051120032	-2.974	3.798
650	923	1.083	0.060321855	-2.808	4.020
700	973	1.028	0.069273267	-2.670	4.211

Activation energies (Electrolyte 1)

$E_{a,LT}$		$E_{a,HT}$	
98.93	kJ/mol	35.94	kJ/mol
1.45	eV	0.36	eV

Electrolyte 2: SDC 80 wt% + NLK 20 wt% composite

T (°C)	T (K)	$1000/T$ (K ⁻¹)	σ_{total} (S/cm)	$\ln(\sigma_{\text{total}})$	$\ln(\sigma_{\text{total}} T)$
250	523	1.912	5.31E-06	-12.147	-5.887
300	573	1.745	8.16E-05	-9.414	-3.063
350	623	1.605	0.0008	-7.131	-0.696
375	648	1.543	0.0045	-5.404	1.070
380	653	1.531	0.0068	-4.991	1.491
390	663	1.508	0.011	-4.510	1.987
400	673	1.486	0.02	-3.912	2.600
410	683	1.464	0.024	-3.730	2.797
420	693	1.443	0.045	-3.101	3.440
450	723	1.383	0.1	-2.303	4.281
500	773	1.294	0.17	-1.772	4.878
550	823	1.215	0.23	-1.470	5.243
600	873	1.145	0.29	-1.238	5.534
650	923	1.083	0.35	-1.050	5.778
700	973	1.028	0.42	-0.868	6.013

Activation energies (Electrolyte 2)

$E_{a,LT}$		$E_{a,HT}$	
140.62	kJ/mol	35.19	kJ/mol
1.45	eV	0.36	eV