The Conductivity of Aqueous K_2CO_3 at Elevated Temperatures and Pressures, Measured using the AC van der Pauw Technique

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Abstract: *Conductivity measurements of aqueous K_2CO_3 were performed using the van der Pauw method and a specially designed sample holder with Pt wires as electrodes. The resistance was measured using alternating current. The conductivity of 10-50 wt% aqueous K_2CO_3 was measured at room temperature and ambient pressure. The conductivity was found to increase with concentration up to 30-40 wt%, and decline at higher concentrations. Furthermore, the conductivity of 5-30 wt% aqueous K_2CO_3 was measured up to 180-200 °C at 30 bar. The highest conductivity measured was 1.34 S/cm at 172 °C for 30 wt% K_2CO_3 (aq). The conductivity was found to increase with concentration and also temperature for 5-15 wt%. For 20 and 30 wt% K_2CO_3 (aq) the conductivity also increased with temperature up to a certain point and then a drop was seen at 150 and 180 °C, respectively. The activation energy was also obtained by fitting the data to a modified Arrhenius equation. The activation energy was found to be in the range 0.14-0.17 eV and did not appear to be concentration dependent.*

Keywords: Conductivity; K_2CO_3; Aqueous solution; Van der Pauw; Electrolysis

1. INTRODUCTION

With the world focusing increasingly on renewable energy sources, an increasing need for energy storage arises. Most sources for renewable energy, such as wind and solar energy, do not generate a steady and controllable energy output, but fluctuate [1]. It is, therefore, necessary to store excess energy so it can be used when needed. One way of storing excess energy is by electrolysis of water. For instance, excess electricity can be used to generate hydrogen, which can then later be used to drive a fuel cell, thereby generating electricity again [2, 3]. Another possibility for storing energy is by co-electrolysis of CO_2 and water. Co-electrolysis using solid oxide electrolysis cells (SOEC) results in synthesis gas (H_2 + CO) which can then be reformed into synthetic fuels (hydrocarbons) such as methanol [4, 5]. There is a constant search for materials and improvements that can make more efficient and cheaper electrolysis cells [2].

Electrolysis at elevated temperatures has the advantage of improved electrical efficiency. In the case of an aqueous electrolyte, both temperatures and pressures must be increased, and, for this, it is necessary to know the electrolyte properties, such as ionic conductivity, thermal expansion, vapor pressure of water, and stability towards phase separation under these conditions. Aqueous electrolytes are known for their high conductivity at lower temperatures, but operation at higher temperatures introduces issues of water management. As $KHCO_3$ (aq) and K_2CO_3 (aq) are already known in literature as electrolytes for reduction of CO_2 at temperatures below 100 °C [6-10] we decided to explore K_2CO_3 (aq) as a potential electrolyte for co-electrolysis at high pressure and temperature above 100 °C. Further, as K_2CO_3 (aq) has a higher conductivity than $KHCO_3$ (aq) the purpose of this study is to explore the properties of K_2CO_3 (aq) at temperatures from ambient to 200 °C.

Although this study covers the properties of the electrolyte as a free flowing liquid, in an application, it is likely that it would be immobilized in a porous medium, as this would make it easier to handle and allow its use in cells similar to those used with polymer electrolytes.

1.1. The van der Pauw technique

The measurement of the ionic conductivity of aqueous solutions

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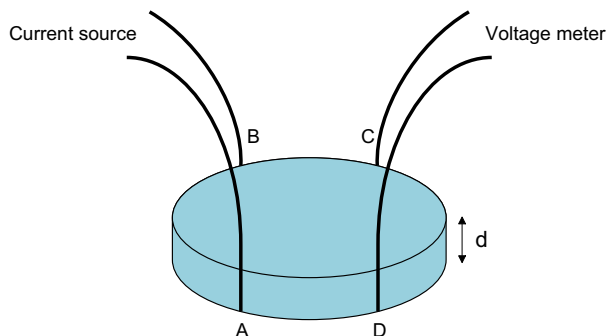 Danish Technological Institute, Gregersensvej, DK-2630 Taastrup, Denmark

Figure 1. Sample with four contacts. Current source and voltage meter are shown on the figure.

Figure 2. Drawing of sample holder used for conductivity measurements.

is usually performed in a dip cell with parallel electrodes made of platinum foil. However, with concentrated solutions of high conductivity where cell resistances are low, the resistance of the leads becomes significant. This can be counteracted by increasing the ratio of cell length to cell area.

Alternatively, the conductivity can be measured using the van der Pauw technique. It is commonly associated with semiconductors and metals [11], but the technique has also been proved to work on electrolyte solutions [12, 13]. The method involves placing four probes at the edge of the sample, as shown in Fig. 1. For the technique to work, the contacts must be sufficiently small, and the sample of homogenous thickness and simply connected (i.e. free of holes). Two adjacent electrodes are used for supplying the current and the other two for measuring the voltage. After this, the connections are rotated 90°, A→B, B→C, C→D and D→A. The voltage/current ratios for the two cases will then be $R_{AB,CD}$ and $R_{BC,DA}$. The measurement does not stipulate that the sample be cylindrical or the electrodes equally spaced around the sample, however this geometry is often chosen for convenience.

The specific resistance of the sample, ρ, is related to $R_{AB,CD}$, $R_{BC,DA}$ and the height of the sample, d, as follows [11]:

$$e^{(-\pi d R_{AB,CD}/\rho)} + e^{(-\pi d R_{BC,DA}/\rho)} = 1 \tag{1}$$

If $R_{AB,CD} = R_{BC,DA} = R$ the equation has an explicit solution [11]:

$$\rho = \frac{\pi d}{\ln 2} R \tag{2}$$

Furthermore, if $R_{AB,CD} \gg R_{BC,DA}$ (if for example, they differ by 20% or less) the following equation can be used [11]:

$$\rho = \frac{\pi d}{\ln 2} \frac{R_{AB,CD} + R_{BC,DA}}{2} \tag{3}$$

However, if $R_{AB,CD} \neq R_{BC,DA}$ the specific resistance can be calculated using the following equation [11]:

$$\rho = \frac{\pi d}{\ln 2} \frac{R_{AB,CD} + R_{BC,DA}}{2} f \tag{4}$$

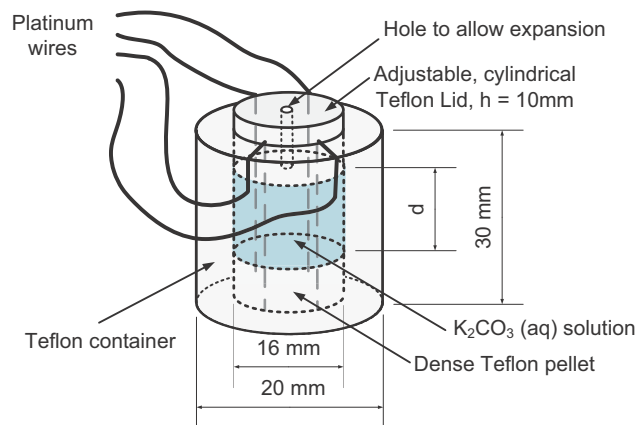where f is a function of the ratio $R_{AB,CD}/R_{BC,DA}$ and can be approxi-

mated by the following equation [11]:

$$f \approx 1 - \left(\frac{R_{AB,CD} - R_{BC,DA}}{R_{AB,CD} + R_{BC,DA}}\right)^2 \frac{\ln 2}{2}$$
$$- \left(\frac{R_{AB,CD} - R_{BC,DA}}{R_{AB,CD} + R_{BC,DA}}\right)^4 \left(\frac{(\ln 2)^2}{4} - \frac{(\ln 2)^3}{12}\right) \tag{5}$$

The specific conductivity is the inverse of the specific resistance:

$$\sigma = \frac{1}{\rho} \tag{6}$$

The advantage of the van der Pauw technique is that the resistance obtained is free of any contribution from the electrodes and only depends on the height of the sample [11]. Although most applications of the technique have been on electronic conductors, using DC, the technique has also been proven to work on electrolyte solutions [12] and solid electrolytes [14], using AC.

2. EXPERIMENTAL

K_2CO_3 (aq) solutions were prepared from K_2CO_3 powder (Sigma-Aldrich, ACS reagent) and Milli-Q water.

A specially designed 4-electrode sample holder was used to perform the measurements. The sample holder consisted of a Teflon cylinder with a lid. The lid was only used for tests at elevated temperature and pressure. The four electrodes were attached to the inside of the cylinder with a Teflon pellet. The lid had a hole to allow for compression upon pressurization and thermal expansion of the liquid upon heating. The lid insured that the liquid filled the cell in all cases. The electrodes consisted of Pt wires. A drawing of the sample holder can be seen in Fig. 2. The height of the solution, d, was approx. 10 mm for all measurements. The uncertainty of the height is estimated to be ~1% as the height could be measured with an accuracy of 0.1 mm.

AC measurements were performed using a Gamry reference 600 or 3000 potentiostat [15].
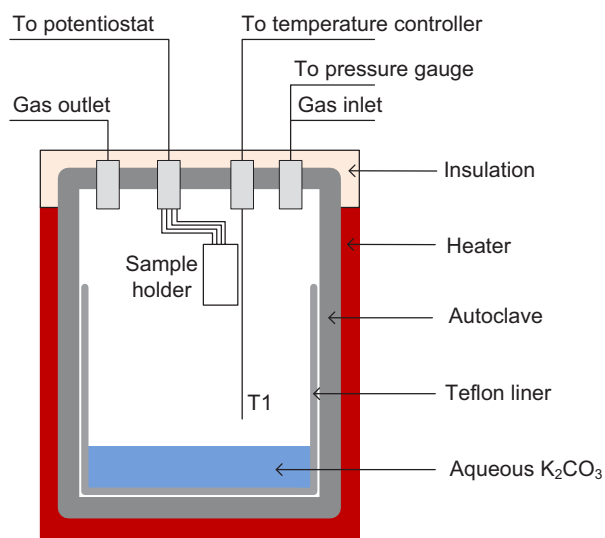
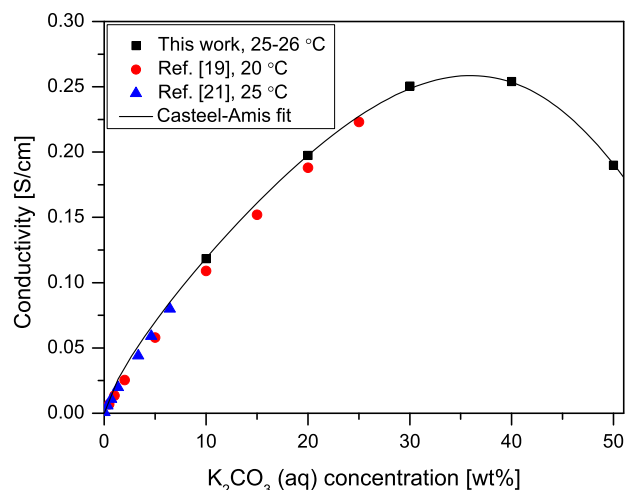Figure 3. Setup overview, T1 = J-type thermo well.

Figure 4. Conductivity of 0.01-50 wt% K_2CO_3 (aq) at ambient temperature. The measured data has also been fitted using the Casteel-Amis equation.

Measurements at ambient temperature and pressure were made in galvanostatic mode with 10 mA amplitude in the range 10 Hz – 10 kHz. Measurements were performed in all 4 possible configurations (where half have identical resistances), by rotating the wires 90° between each measurement. All measurements inside the autoclave were performed in potentiostatic mode and with 10 mV amplitude and in the range 100 Hz – 100 kHz. The measurements were performed with two different configurations at room temperature by making one measurement and then rotating the wires 90°. The measurements at elevated temperature were made with one configuration where the resistance was $R_{AB,CD}$.

The resistance was taken to be the mean of the modulus of the impedance (Z_{mod}) for those measurements for which the phase angle was smaller than ±0.5° for ambient temperature and pressure and smaller than ±1° for elevated temperature and pressure (see for example Fig. 5).

For conductivity measurements under pressure and at elevated temperatures the cell was enclosed in a Parr autoclave type 4760 with 600 ml volume and a Teflon liner. The autoclave was made of Inconel 600 which is known to be very corrosion resistant in alkaline media [16] and also a suitable material when using a steam and CO_2 containing atmosphere [17, 18]. The autoclave was pressurized using nitrogen gas. A heating mantle with a temperature controller was used to heat the autoclave, however, some temperature overshooting was observed. A J-type thermo well was used to measure the temperature inside the autoclave. The sample setup has also been used to measure the conductivity of KOH (aq) [13]. An overview of the setup can be seen in Fig. 3. An aqueous solution of K_2CO_3 with a concentration lower that the one being measured was placed in the bottom of the autoclave in the Teflon liner to prevent water loss from the solution being measured.

The compressibility of K_2CO_3 (aq) solutions should be similar to that of water and sodium chloride solutions, i.e. in the order of 10^{-5} bar^{-1} [19], and the thermal expansion of a 27 wt% K_2CO_3 (aq) solution is < 1.5 % from -15 to 30 °C [20]. Therefore, the effect of pressurization and thermal expansion was considered negligible.

3. RESULTS

3.1. Ambient pressure and temperature

The conductivity of 10-50 wt% aqueous K_2CO_3 at ambient temperature and pressure was measured and compared to literature values [19, 21], see Fig. 4. The resistance was found to be almost identical for the four different configurations so the conductivity was calculated using equation (2) and (6). The average of the conductivity found for each of the four different configurations was defined as the sample conductivity.

The measured values were in good agreement with the literature values. The conductivity appeared to increase non-linearly with concentration and reached a maximum at 30-40 wt% K_2CO_3 (aq). At higher concentration the conductivity decreased again.

It was also found that the conductivity was highly temperature sensitive: a change of only a few degrees had significant effect on the conductivity.

The measured conductivity was fitted to the Casteel-Amis equation [22], using molality instead of weight percent as the concentration. The fit can be seen in Fig. 4 and the values for the fit can be seen in Table 1.

Recently, the general behavior of concentrated electrolytes showing a maximum conductivity at a given concentration has been rationalized by the pseudolattice theory for concentrated electrolytes and ionic liquids [23]. This theory describes concentrated electrolyte solutions and ionic liquids with very strong ion-ion interactions as having a pseudolattice, in which it is necessary to

Table 1. Fitting values for the fit of the measured data shown in Fig. 4. The fit was made using the Casteel-Amis equation, $y = x^a \cdot exp(-b \cdot x^2 + c \cdot x + d)$, where y is the specific conductivity and x is the molality.

a	b	c	d
0.752±0.029	0.015±0.001	-0.062±0.020	-190.725±0.018

Figure 5. Z_{mod} (■ left) and phase angle (▲ right) as a function of frequency for a typical measurement.
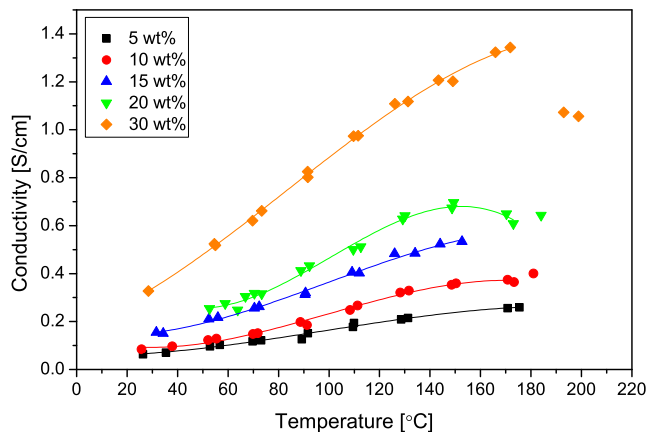

Figure 6. Conductivity of 5-30 wt% K_2CO_3 (aq) from ambient temperature to 180-200 °C. All measurements were performed at 30 bar. The lines are third order polynomial fits made for each concentration from ambient temperature to 180 °C.

have "vacant sites" and as the concentration increases the "vacancy" concentration decreases and the interactions become stronger. This theory has much similarity with ionic conductivity in solids. Janek *et al.* [24] pointed out such similarities almost 20 years ago by describing solids using liquid electrolyte theory. They pointed out that at high concentrations/strong ion-ion interactions the liquid electrolytes behave quite similar to solid conductors.

3.2. Elevated pressure and temperature

The conductivity of 5-30 wt% K_2CO_3 (aq) was also measured from ambient temperature up to 180-200 °C at 30 bar. The difference between the two resistances $R_{AB,CD}$ and $R_{BC,DA}$ measured at ambient temperature was found to be small enough for 5-20 wt% K_2CO_3 (aq) to allow the correction factor, f, to be one. However, the correction factor was applied to the data for 30 wt% K_2CO_3 (aq), after having been determined using equation (5). The correct resistance ($R_{correct}$) was found by multiplying the measured resistance with the average of $R_{AB,CD}$ and $R_{BC,DA}$, divided by $R_{AB,CD}$ all measured at room temperature. The conductivity was found by taking the average of Z_{mod} for all frequencies where the phase angle was smaller than ±1° and then using equation (3) or (4) (assuming $R_{correct} = R_{AB,CD} = R_{BC,DA}$) and (6).

The Z_{mod} and phase angle of a typical measurement can be seen in Fig. 5. It can be seen that Z_{mod} was very stable over the whole frequency range. The figure also shows that the phase angle was smaller than ±2° for the whole frequency range and smaller than ±0.5° in the range 100-20000 Hz.

Figure 6 shows the conductivity of 5-30 wt% K_2CO_3 (aq) at elevated temperature and pressure. It can be seen that the conductivity

increased almost linearly with temperature up to 100-120 °C. In most cases the conductivity also increased with concentration. For 30 wt% K_2CO_3 (aq) a drop in conductivity was seen above 180 °C and for 20 wt% a small drop was seen at 150 °C. The highest conductivity measured was 1.34 S/cm at 172 °C for 30 wt% K_2CO_3 (aq).

The conductivities of 5-30 wt% K_2CO_3 (aq) from ambient temperature to 180 °C have been fitted using a third order polynomial, see Fig. 6. The fits have no particular physical meaning but can be used for estimating conductivities at other temperatures and concentrations than the measured. The estimated conductivity at a range of temperatures can be found in Table 2.

A phase diagram has been calculated using FactSage [25], see Fig. 7. The database Fact53 was used for the calculations and both liquids (except for plasmas), solids, gas and aqueous species were allowed in the calculations. Initially only K_2CO_3 and H_2O were assumed to be present at 30 bar. The calculations assume complete equilibrium. Gasses were assumed to be real and not ideal. Available molar volume data was also included. Calculations were made for 0-100 wt% K_2CO_3 at 0-300 °C.

The phase diagram shows that precipitation of $K_4C_2O_6(H_2O)_3$ (($K_2CO_3)_2(H_2O)_3$) occurs for 30 wt% above 145 °C and that precipitation of K_2CO_3 occurs for 20 wt% above 190 °C, see Fig. 7.

Table 2. Conductivity of 5-30 wt% K_2CO_3 (aq) at various temperatures, calculated from third order polynomial fits. Values are only given at temperatures and concentrations were the system is predicted to be completely aqueous.

	40 °C	60 °C	80 °C	100 °C	120 °C	140 °C	160 °C	180 °C	200 °C
5 wt%	0.08	0.10	0.13	0.16	0.20	0.23	0.25	0.26	0.26
10 wt%	0.10	0.13	0.17	0.23	0.29	0.34	0.37	0.37	0.33
15 wt%	0.17	0.22	0.29	0.36	0.44	0.51	0.56	0.58	0.57
20 wt%	0.27	0.27	0.35	0.47	0.58	0.66	0.67	0.58	N/A
30 wt%	0.41	0.56	0.72	0.88	1.04	1.18	N/A	N/A	N/A

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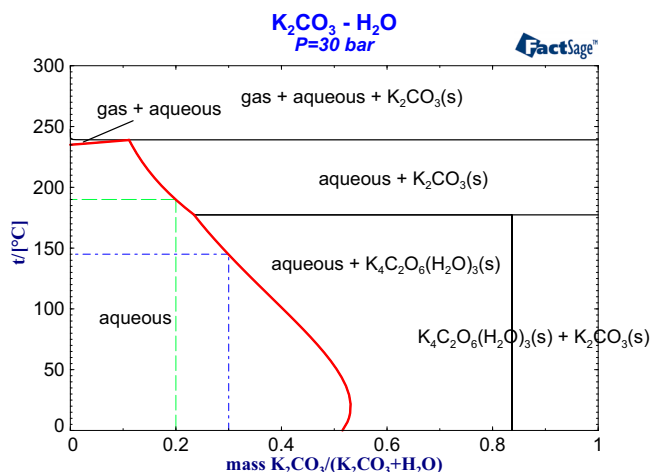*/ J. New Mat. Electrochem. Systems*

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Figure 7. Calculated phase diagram for K_2CO_3 and H_2O at 0-300 °C and 30 bar. The dashed and dash-dot line indicates at which temperature precipitation occurs for 20 and 30 wt% K_2CO_3 (aq) respectively. The thick line shows the limit for the aqueous region.

Figure 8. Arrhenius plot showing $\ln(\sigma T)$ as a function of $1/T$ for 5-30 wt% K_2CO_3 (aq). The lines show the linear fits.

Precipitation would result in fewer charge carriers and therefore a drop in conductivity as seen in Fig. 6. The figure also shows that precipitation of $K_4C_2O_6(H_2O)_3$ $((K_2CO_3)_2(H_2O)_3)$ occurs at concentrations above 50 wt% at room temperature and that the precipitation takes place at lower concentrations with increasing temperature.

3.3. Activation energy

It has been reported that the conductivity of molten salts can be described using an Arrhenius equation [26]. We have found that our measured data can be described using the following modified Arrhenius equation [27, 28]:

$$\sigma = \frac{A}{T} e^{-E_a/RT} \qquad (7)$$

A plot of $\ln(\sigma T)$ as a function of $1/T$ will thus have the slope $-E_a/R$. The modified Arrhenius equation was found to give a slightly better fit than the simple Arrhenius equation with A instead of A/T.

Figure 8 shows $\ln(\sigma T)$ as a function of $1/T$ for 5-30 wt% K_2CO_3 (aq) for temperatures below 150 °C and the corresponding linear fits. The pre-exponential factor (A) and the activation energy (E_a) can be found in Table 3. The fit appears to be very good and the activation energy was in range 0.14-0.17 eV for all the measured concentrations. It can be seen that the activation energy is similar for 5, 15 and 30 wt% K_2CO_3 (aq) and higher for both 10 and 20
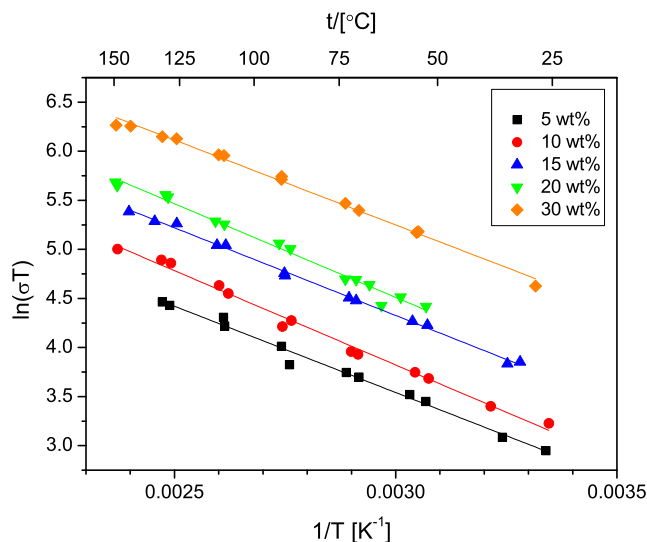
wt%. Furthermore, the pre-exponential factor for 15 wt% K_2CO_3 (aq) is very close to the value for 10 wt% K_2CO_3 (aq) and is therefore lower than expected.

4. DISCUSSION

The difference between the measured conductivity values shown in Fig. 4 and the values found in the literature can be explained by the difference in temperature.

Even though the ionic conductivity may follow an Arrhenius expression over a certain temperature range, this relation may break down at high temperatures. According to Clay *et al.* [26] and the pseudolattice theory [23] there is competition between thermal activation and increased ion-ion interaction with increasing temperature (in the present case, due to the decreasing dielectric constant of water), that results in a conductivity maximum at some high temperature. The drop for 30 wt% K_2CO_3 (aq) seen in Fig. 6 may be explained by this, and it is also reflected in the calculated phase diagram seen in Fig. 7, because eventually at a high enough temperature, when the ionic interaction become strong enough, salt will precipitate. According to the phase diagram precipitation should occur above 145 °C and not 172 °C as seen in Fig. 6. It is possible that the system was not at equilibrium with respect to the water partial pressure or that the measured temperature was not the actual sample temperature. This would lead to precipitation at a higher temperature than expected. However, it might also be that

Table 3. Pre-exponential factor and activation energy including standard error for 5-30 wt% K_2CO_3 (aq). Calculated from a linear fit of $\ln(\sigma T)$ as a function of $1/T$ using $y = a + bx$.

	5 wt%	10 wt%	15 wt%	20 wt%	30 wt%
A/(K·S/cm)	6800±1200	14800±2100	16200±1400	28300±5000	34500±3900
E_a/eV	0.152±0.005	0.166±0.004	0.154±0.003	0.165±0.006	0.149±0.004
E_a/kJ/mol	14.6±0.5	16.0±0.4	14.9±0.2	15.9±0.5	14.4±0.3

the phase diagram is not correct due to uncertainties in the thermo-dynamic values available for this system.

For 20 wt% K_2CO_3 (aq) there appears to be a decrease in conductivity above 150 °C, which is not expected since the phase diagram indicates that precipitation does not occur until above 190 °C. This discrepancy could be due to two effects: i) Temperature overshooting before stabilizing at the desired temperature, as mentioned in the experimental section. ii) Evaporation of water from the sample, which would cause a higher than expected local concentration of K_2CO_3. Both of these effects would cause precipitation and loss of conductivity, and would take some time before reverting to the equilibrium condition.

The measured conductivities are in the range 0.06 to 0.6 S/cm which are comparable to PEM electrolytes with standard and modified Nafion® membranes which usually have an electrolyte conductivity in the range 0.1-0.4 S/cm [28, 29].

The Arrhenius fits are satisfactory and the activation energy is found to be quite low, 0.14-0.17 eV, and does not appear to be dependent on concentration in this case. The values are similar to the values found for Nafion® membranes (approx. 0.1 eV) and for other aqueous solutions [28, 30] and much lower than the values found for typical solid electrolytes, based on zirconium and cerium oxides (0.6-1.0 eV) [31]. The fit was limited to conductivity values obtained below 150 °C due to the loss of conductivity for 20 wt% K_2CO_3 (aq) seen above this temperature. The low pre-exponential factor found for 15 wt% K_2CO_3 (aq) can be explained by the measured temperature being lower than the actual sample temperature due to using a thermo well. If this is the case the actual pre-exponential factor and activation energy are higher. An increased activation energy for 15 wt% K_2CO_3 (aq) would also mean that the activation energy peaks at 15 wt% K_2CO_3 (aq) and would thus be dependent on concentration.

5. CONCLUSION

Aqueous K_2CO_3 solutions have been examined as candidate electrolytes for water CO_2 co-electrolysis cells. Conductivity results indicate that solutions with concentrations of up to 20 wt% can be used at temperatures from ambient to 200 °C and the conductivities obtained are in the range 0.06 to 0.6 S/cm. Therefore, K_2CO_3 (aq) has good potential as electrolyte. The electrolyte also appears to be suitable for applications where thermo-cycling occurs, provided large temperature excursions above the working range are avoided. The small temperature dependence of the conductivity makes pressurized K_2CO_3 (aq) an interesting candidate as a new potential electrolyte at elevated temperatures.

6. ACKNOWLEDGEMENTS

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