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The application of the Wilhelmy balance to the measurement of electrocapillary effects in molten carbonate

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Abstract In this work, the Wilhelmy method is shown to be very suitable for studying electrocapillary effects in molten salts. Unlike the optical methods usually used this method, can easily be used in automated set-ups. High accuracies of 0.3° in the contact angle were easily obtained.

First experiments are reported on the electrocapillary effect on gold in molten carbonate under air. Small changes of 4° to 8° in the contact angle were found for potential excursions of -300 mV. At 650°C a value of $65 \pm 1^\circ$ was obtained at Open Cell Voltage (OCV) which is in good accordance with the values found by Mugikura et al. and Matsumura et al.

The wetting of gold by carbonate decreased at higher temperatures. In the literature, both positive and negative temperature effects have been reported, obtained in different gas atmospheres. Possibly the sign depends on the gas atmosphere used. However, this discrepancy can also be caused by differences in the characteristics of the gold surface used in the different studies.

Key words Wilhelmy balance · Molten carbonate fuel cell · Molten carbonate · Wetting · Electrocapillary effect

Introduction

The molten carbonate fuel cell (MCFC) cathode and anode performance are directly affected by their pore structure and the wetting of the pores by the molten carbonate electrolyte. Wetting and pore structure also control the distribution of the electrolyte among cath-

ode, matrix and anode. Electrolyte distribution is recognised as one of the factors influencing the MCFC lifetime [1, 3]. Hence it is important to quantify the wetting of anode and cathode materials by molten carbonates. This is generally done in terms of the contact angle θ defined as [4]

$$\cos \theta = \frac{\gamma_{\text{ls}} - \gamma_{\text{sg}}}{\gamma_{\text{lg}}} \quad (1)$$

Here γ_{ls} , γ_{sg} and γ_{lg} are the surface tension of the liquid-solid, solid-gas and liquid-gas interface respectively. In the MCFC, a voltage drop over the solid-electrolyte (= solid-liquid) interface exists which affects γ_{ls} due to the electrocapillary effect [5]. Necessarily, θ must be determined as function of potential.

The Wilhelmy balance is a well-known tool for determining wetting properties by measuring the weight of a liquid meniscus on a solid material [4, 6]. From the weight, the contact angle θ can be calculated. Although this method is very suitable for potential-dependent measurements, as is explained below, to our knowledge this option has not been used until now. In this paper we report potential-dependent measurements obtained by the Wilhelmy balance method, performed in molten carbonate under air. In these first experiments, gold instead of Ni and NiO, the actual MCFC anode and cathode material respectively, was used because it is the most stable material in molten carbonate.

Several researchers have already performed wetting experiments in molten carbonate at temperatures around 650°C [1, 2, 7–10]. Two authors measured the contact angle as a function of the potential, using optical measurements [1, 2]. They measured from photographs the height of the meniscus as a function of potential at a flag electrode immersed in molten carbonate. This height can be recalculated to obtain θ . Our method has several advantages compared to this optical method. First of all, no expensive optical windows in this high-temperature environment are required. Secondly, it is laborious to obtain an adequate optical picture of the meniscus as well as to determine θ from it, resulting in few data

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points and a relatively low accuracy. Furthermore, the Wilhelmy balance is very suitable to be incorporated in automated set-ups.

All other studies have been performed using the sessile drop method, which is not very suitable for potential-dependent measurements. Moreover, the accuracy obtained with this method in molten carbonate was relatively low [7–10].

Experimental

Instrumentation

The balance used was a Mettler AE50 S equipped with an IEEE interface, with an accuracy of 0.1 mg and a maximum load of 55 g. The electrochemical measurements were controlled by a Wenking Potentiostat, a Wenking model VSG 72 voltage scan generator and a Wenking model PPT 75 potentiometer, all from Bank Elektronik, Germany. The automated measurement was performed with a computer (IBM PS/2 Model 30) and the TestTeam software package. The potential, current and temperature signals (as potentials) were connected to a switch unit (Philips PM 2120 Universal Switch). This unit sequentially fed these signals to one multimeter (Fluke 45 Dual Display Multimeter), where they were subsequently read and stored by the computer (IBM PS/2 Model 30), see Fig. 1. Then 20 mass measurements were read directly from the balance and their averaged value was stored. Each measurement loop took 50 s.

Electrochemical cell

A schematic representation of the set-up is given in Fig. 1. The carbonate melt is contained in a one-end closed tube of 99.97% alumina with a diameter of 10 cm. The eutectic 62/38 mole% Li/K carbonate mixture is used. The lithium and potassium carbonate powders were stored at 140 °C to minimise the water uptake. The correct mixture is heated in a crucible to 300 °C and kept at that temperature for approximately 12 h, in order to dry the powder further. Next the temperature is raised to 650 °C at a rate of 1 °C/min. The gas composition above the melt was not controlled, i.e. it was air. The electrochemical cell used in these experiments consists

of three electrodes, the working, counter and reference electrode. The counter electrode consists of a cylindrical shaped gold foil which was placed on the bottom and near the inner wall of the alumina crucible. The working electrode is a gold flag electrode attached to a stainless steel rod with a stainless steel clamp and placed in the centre of the crucible. The standard oxygen reference electrode is used [11].

Gold flag preparation

In this work, 99.99% pure gold flags are used, since gold is known to be an inert material in molten carbonate. The dimensions of the two gold flags used in the experiments were $25.10 \times 16.15 \times 0.15$ mm. and $24.90 \times 16.05 \times 0.15$ mm. A minimal surface roughness is required to enable the meniscus to move freely over the surface. Therefore first the gold surface is cleaned using a procedure taken from literature [12]. To obtain smooth surfaces, the gold flags are pressed between two polished chisel steel stamps which were to 1 μm . A pressure higher than the yielding tension of gold of 103 MNm^{-2} was applied [13]. Thus, the gold obtained the shape of the polished metal surface at a microscopic level, determining the surface roughness of the gold flag at 1 μm . Apart from some scratches, probably due to dust particles, the surface looked "mirror like".

Measurement method

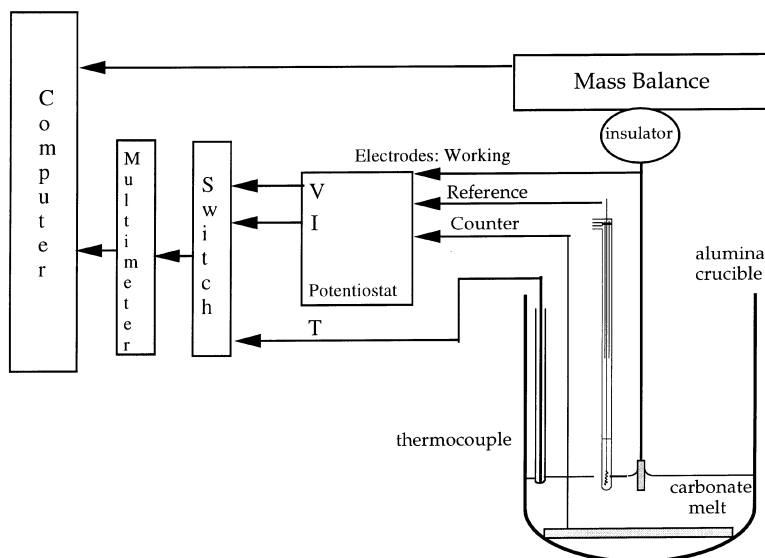
The mass measured by the Wilhelmy balance M_T is determined by the total force (weight) exerted upon it divided by the gravitation acceleration g (9.81 m/sec^2). The total weight is the sum of three different contributions: the weight of the flag electrode and rod $M_e g$, the buoyancy caused by the immersed part of the electrode F_b , and the wetting force due to the liquid meniscus F_w :

$$M_T = M_e + \frac{F_w - F_b}{g} \quad (2)$$

The wetting force is given by [4]

$$F_w = P\gamma_{lg} \cos \theta \quad (3)$$

Fig. 1 Schematic representation of the experimental set-up



in which P is the perimeter of the sample and γ_{lg} the surface tension of the liquid-gas interface. Both the buoyancy and the mass of electrode and rod do not depend on the voltage applied. Therefore it is convenient to write

$$M = M_T - M_e + \frac{F_b}{g} = \frac{P\gamma_{lg}}{g} \cos \theta \quad (4)$$

The contact angle θ can be expressed as

$$\theta = \arccos \left[M \left(\frac{P\gamma_{lg}}{g} \right)^{-1} \right] \quad (5)$$

The value of γ_{lg} for molten carbonates can be obtained from the NIST Database and is 0.20 ± 0.05 N/m, depending on temperature and the carbonate mixture [14]. The perimeter P is (in the order) of 0.032 m in our case. Due to the electrocapillary effect, γ_{ls} and thus the $\cos \theta$ factor in the wetting force (see Eq. 1) varies when the potential is changed. The maximum boundaries for $\cos \theta$ are $+1$ for a completely wetted and -1 for a totally non wetted surface. This corresponds to a change of M between -652.4 and $+652.4$ mg, as can be calculated from Eq. 4 using $P = 0.032$, $\gamma_{lg} = 0.2$ N/m and $g = 9.81$ m/s².

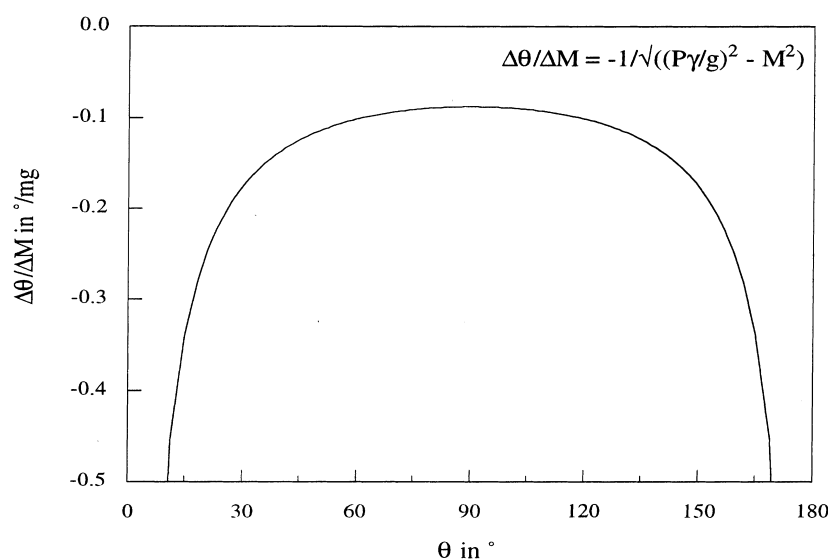
The accuracy in θ as a function of the accuracy in M is obtained by differentiating Eq. 5 with respect to M :

$$\frac{d\theta}{dM} = \frac{-1}{\sqrt{\left(\frac{P\gamma_{lg}}{g}\right)^2 - M^2}} \quad (6)$$

In Fig. 2, this relation is plotted as function of the contact angle (in $^\circ$) in $^\circ/\text{mg}$. The maximum accuracy is obtained for $\theta = 90^\circ$ and can be calculated by inserting $M = 0$ in Eq. 6:

$$\frac{d\theta}{dM} = \frac{g}{P\gamma_{lg}} \quad (7)$$

Fig. 2 Accuracy of θ in $^\circ/\text{mg}$ as a function of the measured contact angle



which in our case yields -0.0015 rad/mg ($0.09^\circ/\text{mg}$). The accuracy improves hyperbolically with increasing perimeter P . Furthermore, liquids with a high liquid/gas surface tension yield a higher accuracy. Figure 2 shows that, for a large range of contact angles between 60° and 120° , the accuracy in θ in $^\circ$ is better than or equal to 0.1 times the error in the mass M in mg. In principle, the accuracy of the balance being 0.1 mg, accuracies up to 0.01° can be obtained. For small and large contact angles, i.e. very well and very badly wetted surfaces respectively, the accuracy in θ becomes much smaller.

Results and discussion

The results are presented in two subsections. In the first, the electrocapillary effect as measured with the Wilhelmy balance on gold in molten carbonate is presented. In the subsequent section, the effect of temperature on the contact angle at Open Cell Voltage (OCV) is discussed.

Electrocapillary effect

In Fig. 3 the mass as function of the potential over the gold-carbonate interface is shown recorded at 600°C under air. The measurement was started at OCV and only potentials more negative than the OCV value were used. Then also a faradaic current due to the oxygen reduction passes through the electrochemical cell. Since the scan rate was $25 \mu\text{V/s}$, a quasi-steady-state polarisation curve was obtained, which is included in Fig. 3. Here we will not discuss the electrochemical part of the measurement but concentrate on the electrocapillary effect. With Eq. 5 the contact angle can be calculated from the measurement in Fig. 3. Values for γ_{lg} are needed, which are listed in Table 1, for three temperatures. They were calculated by linear interpolation from

Fig. 3 Measured weight of the carbonate meniscus at gold surface and current as functions of potential at 600 °C under air

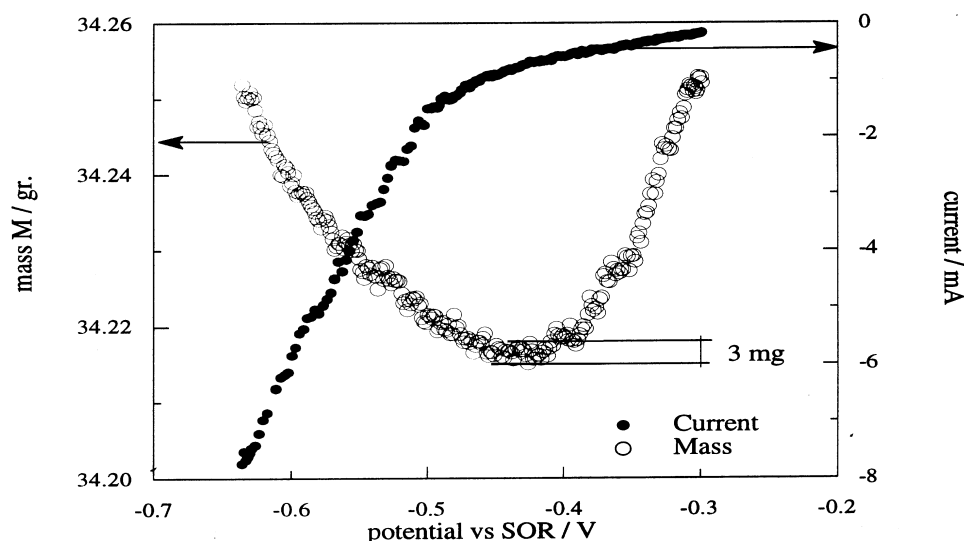


Table 1 γ_{lg} of 50/50 and 70/30 mole% Li/K carbonates at different temperatures taken from [12] and values for 62/38 mole% Li/K calculated by linear interpolation

T (°C)	γ_{lg} N/m		
	50/50 Li/K	70/30 Li/K	62/38 Li/K
600	0.195	0.206	0.201
650	0.193	0.204	0.199
700	0.191	0.203	0.198

values listed in the NIST database for the 50/50 mole % Li/K and 70/30 mole % Li/K mixtures [14].

The contact angles as a function of potential are shown in Fig. 4 together with the measurement at 650 °C and 700 °C. For each temperature a small effect of the potential on the contact angle of 4° at 600 °C, 6° at 650 °C and 8° at 700 °C is observed for potential changes of roughly 300 mV from OCV. Also Mugikura and Matsumura found changes in the contact angle of 4°

and 5° at 600 °C and 650 °C respectively for the same potential change [1, 2]. As an illustration, the contact angles obtained by Mugikura in a $pO_2 = 0.15$, $pCO_2 = 0.3$ and $pN_2 = 0.55$ gas atmosphere are included in Fig. 4.

The noise in the mass measurement could be reduced to 3 to 5 mg by the averaging of 20 mass measurements. This noise level at these θ values leads to an accuracy in θ of 0.3° to 0.5°, as was explained in the former section. These measurements clearly indicate that it is possible to obtain quite accurate measurements of the contact angle with our method, contrary to the optical methods used before in which accuracies of only 2° were obtained as indicated in Fig. 4 [1, 2].

Contact angles at OCV and temperature effect

The contact angles measured at OCV are listed in Table 2. The value at 650 °C ($64 \pm 0.4^\circ$) is in good

Fig. 4 Contact angle of molten carbonate on gold as a function of potential for 600, 650 and 700 °C recorded under air

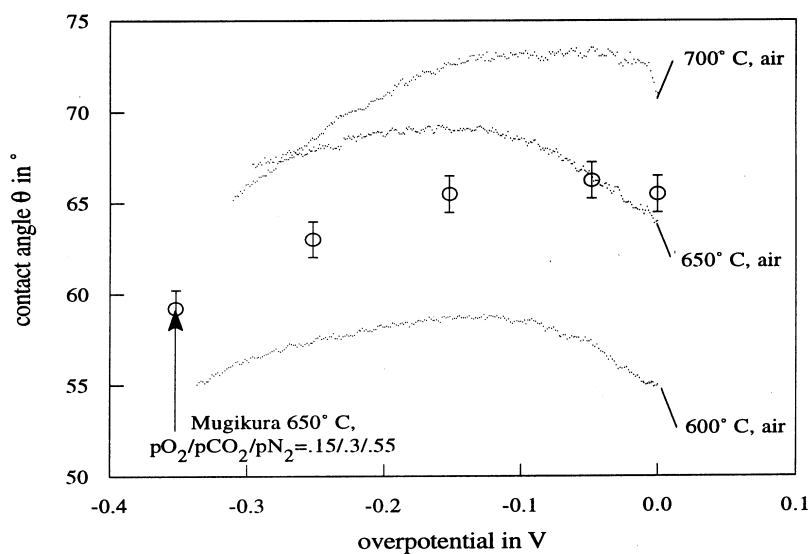


Table 2 Contact angles at OCV for different temperatures under air obtained from two different experiments compared with literature data obtained in several O₂, CO₂ and N₂ containing gas atmospheres

<i>T</i> (°C)	<i>θ</i> (Fig. 4)	<i>θ</i> (Fig. 5)	<i>θ</i> Mugikura [2]	<i>θ</i> Matsumura [3]
600	54 ± 0.3°	55 ± 0.2°	70 ± 2°	–
650	64 ± 0.3°	66 ± 0.2°	67 ± 2°	62 ± 2°
700	71 ± 0.3°	71 ± 0.2°	–	–

agreement with those of Matsumura (62 ± 2°) [2] and Mugikura [1] (67 ± 2°). The latter were obtained in several O₂, CO₂ and N₂ containing gas atmospheres, indicating that wetting does not depend strongly on the gas composition. At 600° a contact angle of 54 ± 0.4° is found at OCV, indicating better wetting (lower contact angles) for lower temperatures. Mugikura obtained higher contact angles for lower temperatures, e.g. 70 ± 2° at 600 °C [1]. However, he also reports a lower contact angle for a lower temperature in a 100% CO₂ atmosphere.

Also in other literature different temperature behaviour is reported with both increasing as well as decreasing contact angles with increasing temperature [1, 7, 8]. Maybe the temperature effect is different in different gas compositions. However, also effects of (changes in) the surface conditions can be responsible for these discrepancies. The surface characteristics of the sample, such as surface roughness, impurities, oxide formation etc., are known to have a large influence on the contact angle [4, 6]. To reconfirm our results the contact angle at OCV was measured as a function of temperature at a fresh gold surface, and the result is depicted in Fig. 5. Clearly again an increasing contact angle with increasing temperature is observed. Two different regions with apparent linear relations are ob-

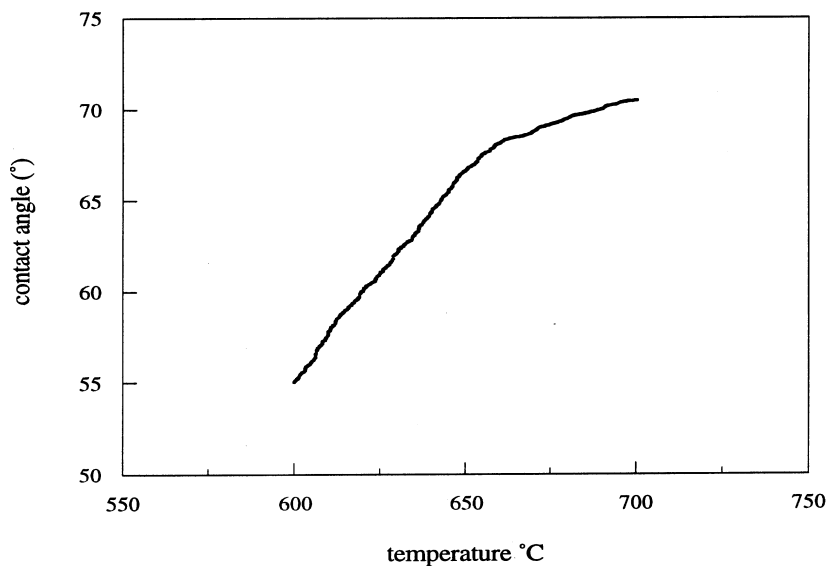
servable. One in which the contact angle depends more strongly on the temperature from 600 to 660 °C with a slope of 0.22°/°C, and one between 660 and 700 °C having a slope of 0.06°/°C. The nature of the splitting of this relation into two temperature regions is not known. The values for the contact angle at OCV obtained in this new experiment are in good accordance with the values of the former experiments, as shown in Table 2. At 650 °C a value of 66° was found as compared with 64° in the first experiment, indicating that the systematic error, of only 1°, in the experiments is larger than the measurement accuracy.

Conclusions

We showed that the Wilhelmy balance is a very suitable method of studying the electrocapillary effect in molten carbonate. A high accuracy of 0.3° was obtained, compared to the ± 2° accuracy obtained by the optical methods used until now [1, 2]. Reproducible values for the contact angle at OCV at different temperatures were obtained. Our first results on the electrocapillary effect on gold in molten carbonate under air were in accordance with literature data available so far. The small changes in the contact angle of ± 4° at 600 °C to ± 8 at 700 °C during negative potential excursions of 300 mV could clearly be observed.

We found a positive effect of temperature on the contact angle, which means that wetting of gold by carbonate decreases at higher temperatures. In the literature, both positive and negative temperature effects have been reported. This discrepancy can possibly be explained by differences in the gold surface characteristics, which are known to have a large effect on the wetting behaviour. Another explanation would be that the sign depends on the gas atmosphere used.

Fig. 5 Contact angle molten carbonate on gold at OCV as a function of temperature recorded under air



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