

A robust methanol concentration sensing technique in direct methanol fuel cells and stacks using cell dynamics

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H I G H L I G H T S

- The electrochemical sensing method can estimate methanol concentration accurately without sensing devices.
- Temperature and degradation effects on the voltage responses are corrected with the newly proposed formula.
- Measurement procedure and data from the single cell and stack experiments are statistically validated by the refractometer.

A R T I C L E I N F O

Keywords:

Direct methanol fuel cell
Methanol concentration
Sensing method
Electrochemistry

A B S T R A C T

The electrochemical behaviour of direct methanol fuel cells (DMFCs) is sensitive to methanol concentration; thus, to avoid external sensors, it is a promising candidate to monitor the concentration of methanol in the fuel circulation loop, which is central to the efficient operation of direct methanol fuel cell systems. We address this issue and report on an extremely robust electrochemical methanol sensing technique that is not sensitive to temperature, cell degradation and membrane electrode assembly (MEA) type. We develop a temperature independent empirical correlation of the dynamic response of cell voltage to step changes in current with methanol concentration. This equation is successfully validated under various operating scenarios at both the single cell and stack levels. Our sensing method achieves an impressive accuracy of ± 0.1 M and this is expected to increase the reliability of methanol sensing and simplify the control logic of DMFC systems.

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Introduction

The power demands of telecommunication towers [1], surveillance cameras or portable generators for civil engineers [2] are growing globally. In many cases, electric consumers require continuous power without having access to an electrical grid. To use wireless devices such as smart phones securely, reliable backup power systems are required. A direct methanol fuel cell (DMFC) system as a backup power offers a viable solution to this problem due to its high energy storage to cost ratio [3].

For the seamless and efficient operation of a DMFC system, controlling the methanol concentration in the fuel circulation loop is important [4]. Yet, it is a challenging task as a highly concentrated solution from the fuel reservoir, often 100 m % methanol, needs to be diluted to low concentrations of ca. 0.5–1 M solution (<3 m % methanol), and as sensors for control in the usually small, outdoor and low cost systems should be robust, fast, low cost and very small. The methanol concentration in the circulating fuel stream is continuously measured with a suitable methanol sensor and fed to the control logic. The control logic then calculates for the stable operation of the DMFC system, the amount of neat methanol to be mixed with the unreacted methanol stream from the anode outlet and the excess water captured at the cathode outlet. There are two types of methanol sensors that can be used for this purpose, namely physical and electrochemical methanol sensors. Physical methanol sensors are often employed in commercial DMFC systems [5]. However, physical methanol sensors are very sensitive and vulnerable to temperature changes, pressure changes and gas bubbles in fuel stream which results in measurement error. In addition, physical sensors are expensive and bulky. In this respect, an electrochemical methanol sensor offers several advantages and is more reliable. Electrochemically sensing the methanol concentration is a technique where in the methanol concentration is determined from the characteristic behaviour of cell potential when subjected to a certain current profile. In general, electrochemical sensing may be integrated in the DMFC system in two ways. First, from the current voltage characteristics of additional electrochemical sensing cells incorporated in the anode loop (in line sensors (ILS)) and second, from the current voltage characteristics of the DMFC cell/stack itself. As no sensor is required for the latter type of sensing, it is referred to as sensor less concentration control (SLCC) or the in situ sensing technique. This option does not add additional cost and volume and is thus attractive. In the former type of sensor, an additional sensing cell is either MeOH/O₂ [6] or MeOH/H₂ [7–9]. In the MeOH/O₂ cell, the OCV or short circuit current or potential at constant current serves as the concentration indicator. In an MeOH/H₂ cell, the methanol oxidation current under constant potential serves as the concentration indicator. Because of the inherent advantage of SLCC over the ILS technique in simplifying the balance of plant and reducing the cost and weight of DMFC systems, we only focus on and discuss the SLCC technique in this article; however, findings are transferable.

Few papers on SLCC technique have been published thus far. For the estimation of methanol concentrations, most of the literature on the SLCC technique rely either on estimation

based on the comparison of voltage/current/temperature characteristics to pre generated reference databases [10–15] or on estimations based on live feedback of voltage/current/temperature [16–21]. Dynamic behaviour of the cell was also used to estimate methanol concentration, as reviewed in Ref. [22]; this included the response to sinusoidal current changes, as in impedance spectroscopy or based on the non linear frequency response of a DMFC [23] and the response to a step change in current or voltage, or even sweep voltages [21,22].

Ha et al. [12] created a database by carrying out experiments to estimate methanol consumption rates by CO₂ measurements at the cathode while Arisetty et al. [13], recorded DMFC voltage at various current and methanol concentrations. A more extensive database was created by Chiu and Lien [11] by generating 3D surface concentration plots of DMFC voltage with respect to the current and temperature. Shen et al. [14] improvised Chiu and Lien's algorithm by incorporating the degradation rates.

Zenith and Krewer [17] demonstrated a sensor less feed forward control of methanol concentration with the help of a model and experiments on a complete DMFC system consisting of necessary auxiliary units such as cooler, degasser, mixer, condenser etc. The feed forward control was able to maintain the operating concentration within 8% error. However, feedforward is always prone to external errors or changes due to degradation. Measurements are thus un avoidable for reliable sensing. Chang et al. [16,19,20,24], over their several publications, described a control algorithm based on the discrete time fuel injection feedback method. As the reference control parameter in their algorithm always remains the same with each feedback cycle, the algorithm may accumulate errors with each cycle and the fuel cell eventually ceases to function. The algorithm reported by Lian et al. [18] is more adaptive or self corrective meaning that the control parameter takes up a new reference value with each feedback cycle. Such types of control are not affected by cell degradation and temperature variations but nevertheless it takes a long time to adjust the methanol concentration to the right value. This occurs because there is no direct linear correlation between the control parameter (often voltage) and methanol concentration and it takes several feedback cycles to attain the optimal methanol concentration in the anodic loop.

One of the key advantages of database based sensing is that since the concentration is adjusted according to the actual measured data, the adjustments are more realistic and the response time for achieving the desired concentration is expected to be faster. A major disadvantage is that each stack must be calibrated prior, via many experiments; degradation effects are also not easy to incorporate. Even when the degradation rate is considered, as reported by Shen et al. [14], the algorithm can only be applied to other stacks if all of them have similar degradation rates.

In the feedback type of sensing, although cell degradation and temperature variation do not affect the sensing, the concentration adjustment is performed on more unrealistic values and the response time is long, which can lead to stack instability [25].

In summary, for the successful operation of a sensor less DMFC system, three challenges can be identified from the

literature. These are the minimization of the number of experiments to create a database, incorporation of the degradation effects without having to perform degradation studies and temperature effect nullification. In this paper, we address these challenges and present a sensing technique that requires a database of very few experiments. Typically, the number of experiments is reduced at least three times compared to the literature, as our sensing technique is temperature independent. The sensing principle is based on the correlation between the voltage overshoots (which occur during a step reduction in the cell current) to the methanol concentration as reported for the first time in Krewer et al. [22]. In the following, we significantly extend this first proof of concept with studies to temperature, age, cell design, cell number, and especially robustness of the methodology. We present and validate the sensing methodology in single DMFC and also in a scaled up DMFC stack. Moreover, with our method, no prior knowledge of the degradation rate is required and it is applicable to MEAs with different catalyst layers and membranes.

Sensing method

Concept of sensing

When either the cell is subjected to a step change in the methanol concentration [26–28] or to a step decrease in the current value at a given methanol concentration [22,29], the cell potential was found to overshoot before arriving at new steady state value. In prior work on current induced voltage overshooting [30], Krewer et al. showed that overshooting in a DMFC is caused by the interplay between the fast water chemisorption on ruthenium, the slow methanol partial oxidation to a strongly adsorbed CO* species on platinum, and slow oxidation of the adsorbed species. As methanol oxidation depends on methanol concentration, the dynamic response of the cell potential is sensitive to the methanol concentration and its distribution in the electrode.

Krewer et al. [30] used a DMFC model with three step reaction kinetic model identified by means of electrochemical impedance spectroscopy (EIS) [31]. Using a DMFC model, they showed that the interaction of reaction steps at the surface of the anode results in a voltage overshoot and relaxation behaviour within the first 5 s. Slowing down the methanol partial oxidation by decreasing the methanol concentration, changed the signal.

A peculiarity of this was that the voltage response was very nonlinear, i.e. linear methods like EIS are not suitable for this analysis. In depth studies were therefore conducted with an explicit nonlinear method and a nonlinear frequency response analysis, which better enables the investigation of the typical time constants of the dynamic response of the anode. Studies on the methanol sensitivity of this dynamic signal revealed a monotonous correlation of methanol concentration and nonlinear frequency response around ca. 1 Hz [23]. Thus the method was suggested as being suitable for methanol sensing. However, nonlinear frequency response analysis may require too much time and a special hardware to produce and detect nonlinear sinusoidal signals. In contrast,

step changes in current which cause nonlinear voltage responses that can be easily realized with existing hardware, and the signal is also sensitive to methanol. No in depth sensing studies have been presented in the literature thus far. Furthermore, it remains to be seen if the method is sufficiently robust during cell aging and when transferring to the stack level. These questions are addressed in this study. Our method of methanol concentration sensing is an extension of this work wherein the cell operation is interrupted with a defined procedure which lasts for only few seconds. It contains a defined load change to cause an overshooting whose magnitude, φ is used to estimate the methanol concentration. As the DMFC system is usually combined with batteries for the startup process, a short term interruption for causing and analysing an overshoot is plausible. Fig. 1 shows the working concept of how the sensor can be implemented in real DMFC systems for practical application. The voltage response to an applied step change in current is measured by a potentiostat or other voltage meter. Here, the values of peak voltage, V_{peak} and φ are compared with a reference database and the methanol concentration is empirically determined with the equation (presented in the results and discussions). The concentration information is relayed to the control logic and, depending on the estimated concentration value, an appropriate flow rate command is given to the fuel and circulation pumps in order to keep the methanol concentration in the anode loop to the desired level. However, to apply these results in practical systems, calibrations should be periodically carried out, otherwise it could result in a biased estimation of the methanol concentration, which can be detrimental to the control of entire systems.

In this study, an empirical equation is suggested to estimate the methanol concentration without any further calibrations apart from the initial one. This simple methodology can reduce the component costs of the system and simplify its composition, excluding concentration sensors. This conceptual methodology is validated with a single cell and scaled up stack.

Measurement procedure

Our procedure for sensing has been developed by investigating the response of the voltage overshoot magnitude, φ and V_{peak} to parameters like initial current i.e. the current before the step decrease, current step size, anode flow rate and cathode flow rate. In brief, we found a low initial current of 0.1 A/cm², the step size of 0.05 A/cm², the anode flow rate of >0.11 ml/min cm² and the cathode flow rate >10 ml/min cm² to be the best values for obtaining a large and reproducible φ . Further steps and a defined protocol was found to be necessary to improve measurement results. The protocol for conducting the concentration measurements is listed in Table 1. The respective flow rates, currents, and the voltage response is exemplarily depicted in Fig. 2.

The measurement steps follow:

1. Normal operation (29 min)
2. High flow rate purging (20 s)
3. Current step overshoot measurements (10 s)
4. Restoring as same as normal operation (30 s)
5. Load breaking procedure (28 s)

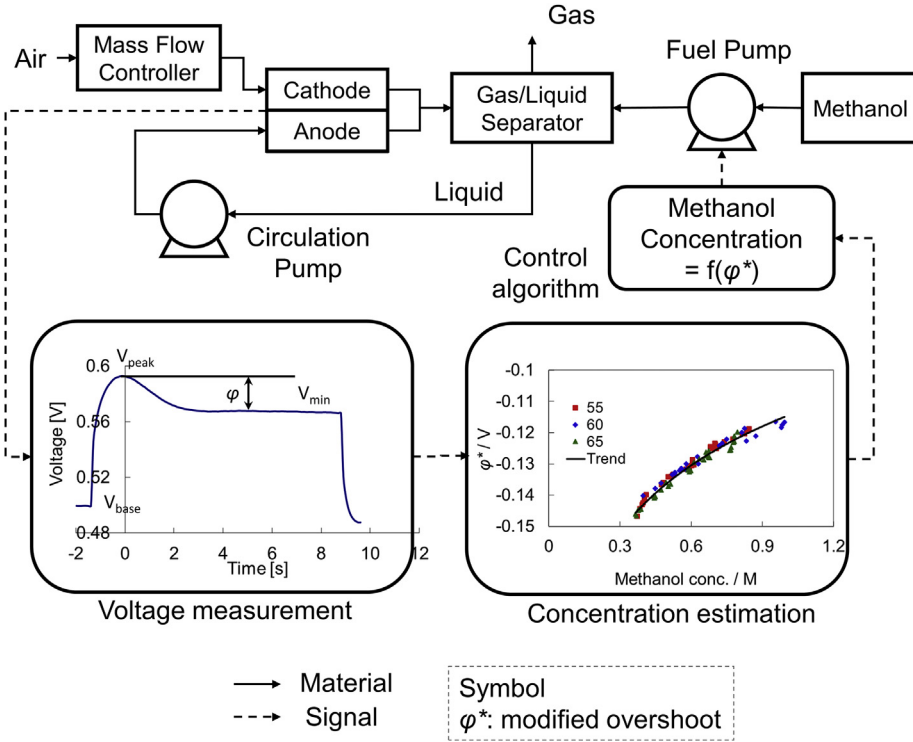


Fig. 1 – DMFC system incorporating sensing technique based on overshooting principle. The voltage response of a stack to an applied step change in current is measured by a potentiostat. V_{base} is the voltage before step current, V_{peak} is the highest voltage which reaches after step decrease in the current and V_{min} is steady state voltage after step current. From this information, the methanol concentration is estimated according to Eqs. (2) and (3) (described in results in discussion). This information is communicated to the fuel pump which accordingly dilutes the neat methanol to the desired operating methanol concentration.

Table 1 – Normal operating procedure of DMFC single cells.

Step No.	Cell current [A/cm ²]	anode flow rate [ml/min cm ²]	cathode flow rate [ml/min cm ²]	duration [s]
1	0.1	0.22	10	1740
2	0.1	0.3	30	20
3	0.05	0.3	30	10
4	0.1	0.22	10	30
5	Load breaking procedure			28

The first step is normal operation for about 29 min with set flow rates in the anode and cathode. This is the normal operating modus of the fuel cell. One minute before the concentration measurement, in step 2, the flow rates are set to higher values for 20 s. This is done to obtain large and reproducible values of φ , especially to remove water drop lets or bubbles that may cause fluctuations, and to obtain homogeneous concentrations in the electrodes. Then the current steps down to half of the normal value in step 3. This produces the evaluated overshoot. In the fourth step, the flow rates are returned to normal values before the load breaking procedure in step 5, a typical procedure to keep DMFCs active.

Cell deactivation is caused by oxide formation on the surface of the Pt catalyst at the cathode. Fortunately, the deactivation is temporary and reversible, and performance can be recovered by air starving the cathode for a few seconds by

means of the so called load breaking procedure (step 5) in Table 1 [32]. During the load breaking step, the current and air flow rate is dropped to zero for a few seconds before the air flow rate is again increased to higher values while retaining the methanol flow rate as constant throughout the entire load breaking step. This is done to reduce the PtO to Pt at the cathode, first by allowing more methanol to crossover at zero current and no cathode flow rate, and second by converting all of the methanol to CO₂ and H₂O by switching the cathode flow rate to high values after a few seconds. In our studies, load breaking was periodically carried out every 30 min.

The voltage response during steps 1–5 is shown in Fig. 2. At the third step, the voltage overshoot is observed (in the red dash circle). A typical increase to a voltage maximum takes 1 s, followed by a slower relaxation period of 1–5 s to the new steady state voltage. The time during which the voltage signal relaxes depends on cell size. The voltage response of single

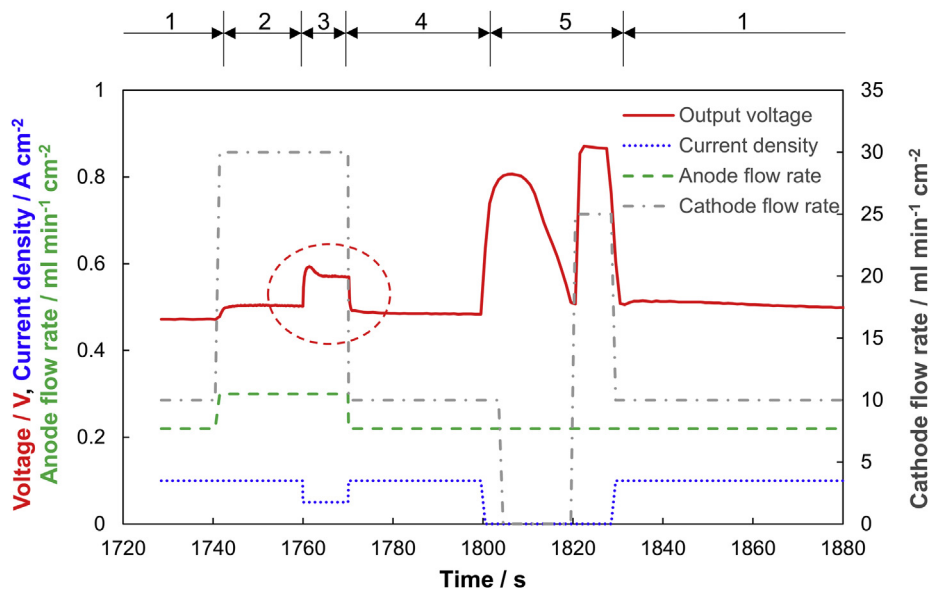


Fig. 2 – Exemplary voltage profile under normal operating procedures with divided steps as explained in Table 1.

cells with a small area takes less than 2 s. Larger cell configurations, such as stacks, need more than 3 s to stabilize voltage.

Experimental set up

Single cell

To construct a single cell, Johnson Matthey (JM M243) and Solvico MEAs (Greenery D300E) with PtRu as the anode and Pt as the cathode catalyst were assembled in an in house constructed cell hardware. The MEA was sandwiched between two machined graphite plates supported by two steel end plates. Cell temperature was controlled with heating cartridges placed inside the steel plates. The active area was 17.64 cm². Methanol solution and air were supplied by a WonATech test station (SmartA, WonATech, South Korea). The methanol concentration were varied between 0.4 M and 0.8 M and at each methanol concentration, corresponding overshoot values were recorded. The voltage response to the step changes in the parameters like current, anode and cathode flow rate were recorded every 0.1 s using Basytec (CTS, BaSyTec GmbH, Germany). The concentration of supplied methanol solution was periodically verified by a refractometer (ATAGO 5000+, ATAGO, Japan).

Stack

A similar composition of Johnson Matthey MEAs as for the single cells were used in a five cell stack except that the active area was 315 cm², to imitate a full stack in an actual DMFC system in the kW class. Methanol solution and air were supplied by a WonATech test station (SmartB, WonATech, South Korea). Similar to single cell, the voltage response was recorded every 0.1 s by the WonATech test station. There is a significant difference between the operation of lab scale single cell and actual DMFC system. The single cell was measured with an

open loop configuration, where a methanol solution was used once and discarded from the anode outlet. It suffices to heat the entire cell with two end plates. In a stack, this heating is not sufficient due to the multiple cells with a high heat capacity; and, additionally, the inlet methanol solution must be heated to maintain the desired temperature in the cells away from the end plates. Three thermocouples were used to monitor the temperature of the air at the cathode outlet. To close the gap between the stack and real DMFC system, the stack was also operated in a closed loop configuration. Here, the methanol anode outlet was circulated back to the anode inlet after replenishment with fuel/water. Hence, the fuel pump, water pump, gas/liquid separator, filter and density meter as a concentration sensor were added to the anode loop. A gas/liquid separator was used to separate the methanol solution and CO₂, as well as a filter to block particles dislodged from the catalyst layer. Finally, to be able to validate the concentration sensing technique, a density meter (MCS, ISSYS, U.S.A.) was used to measure the methanol concentration. The setup resembles thus the one in Fig. 1. The measurements from the density meter or the refractometer were compared with the estimated concentration from the cell dynamics.

Results and discussions

For an accurate measurement of methanol concentration from φ and V_{peak} , two criteria must be met: a) the φ should be large and reproducible with small error bars at all operating conditions and during any stage of a cell's life; b) φ should ideally be sensitive to only methanol concentration. However, neither of the above conditions were practically met and we found that φ was sensitive to many operating parameters as depicted in Fig. 3. While some operating parameters like initial current, step current, the methanol flow rate and air flow rate were simply kept constant, eliminating the other effects such as deactivation, degradation and temperature was not straight forward. As discussed above in section [Measurement](#)

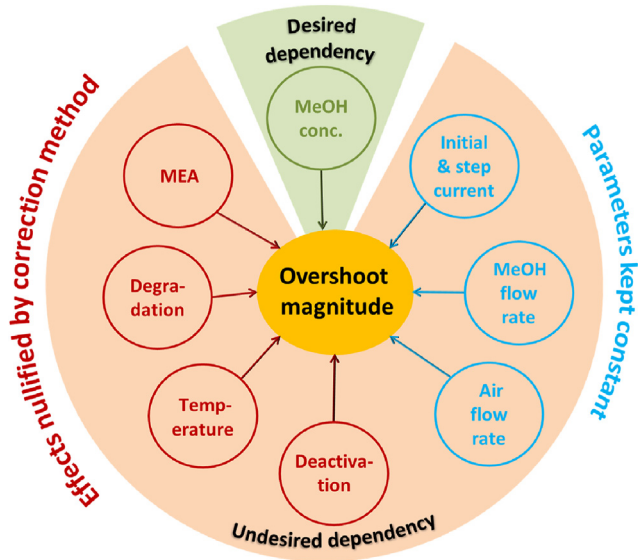


Fig. 3 – Parameters influencing the overshoot magnitude and in turn the sensor accuracy.

procedure, the anode flow rate and cathode flow rate were maintained high enough to be optimize Δi and i_0 such that the φ were large and reproducible. In the following sections, the strategies for the systematic elimination of deactivation, degradation and temperature effects are shown in order to keep φ within a given range, such that the estimation accuracy is better than ± 0.1 M. An accuracy better than ± 0.1 M seems to be a reasonable target considering the accuracy of many commercial sensors, which are around 0.1 M e.g. the density meter of Issys [25].

In the following, we first discuss single cell measurements, then in section [Stack](#) stack measurements.

Single cell

Although load breaking helps in recovering the temporary loss in performance, it does not improve long term performance degradation. DMFCs are known to slowly and permanently

degrade apart from fast temporary deactivation. The evolution of the base voltage vs. time indicates the severity of the degradation in [Fig. 4a](#). In a span of 300 h the cell voltage was reduced by circa 15 mV. Most of the voltage loss occurred in the first 75 h. This trend is similar for other characteristic voltages, namely V_{peak} , V_{min} , seen in [Fig. 4a](#) and φ in [Fig. 4b](#). Although the variance in V_{peak} , V_{base} and V_{min} is higher in magnitude compared to the variance in φ , φ still drops by 7.6 mV within the first 75 h and the difference between the maximum and minimum φ is 9 mV. Such large variation would be catastrophic for sensor accuracy and may cause the concentration estimation to have offset more than 0.2 M. However, the similar trends of V_{peak} , V_{min} , V_{base} and φ can be exploited to create an empirical relationship between overshooting φ and concentration. As the goal is to obtain insignificant variance in φ values with respect to time, a fraction of either V_{peak} , V_{min} or V_{base} can be subtracted from the φ values. This allows us to represent the φ values in a fairly simple formula

$$\varphi^* = \varphi \frac{V_{peak}}{3.75} \quad (1)$$

The fraction of 1/3.75 is found to be optimal for minimising the variance when using V_{peak} . A similar fraction values can be used throughout the entire operation period, independent of the degradation rate. This fraction will have a different value when, for example, V_{base} is used to nullify the variance in φ .

[Fig. 5](#) shows the percent deviation of φ from φ^* with respect to the mean value of $\bar{\varphi}$ and φ^* , over the full measurement time (0–300 h). It is calculated by (measured value – mean value)/mean value. Even when the φ is relatively stable, i.e., after 50 h, the percent deviation from the mean value is still 20%. This directly translates into a measurement error of 20% in the methanol concentration measurement when φ is used as an indicator for methanol sensing. On the other hand, the variation in φ^* is only $\pm 1.5\%$, suggesting that the concentration detection error will be only $\pm 1.5\%$. φ^* seems to be highly stable, especially when the corresponding φ has a large difference, for example in the first 50 h. This indicates that φ^* can completely eliminate the effects of degradation and does not affect the estimation accuracy.

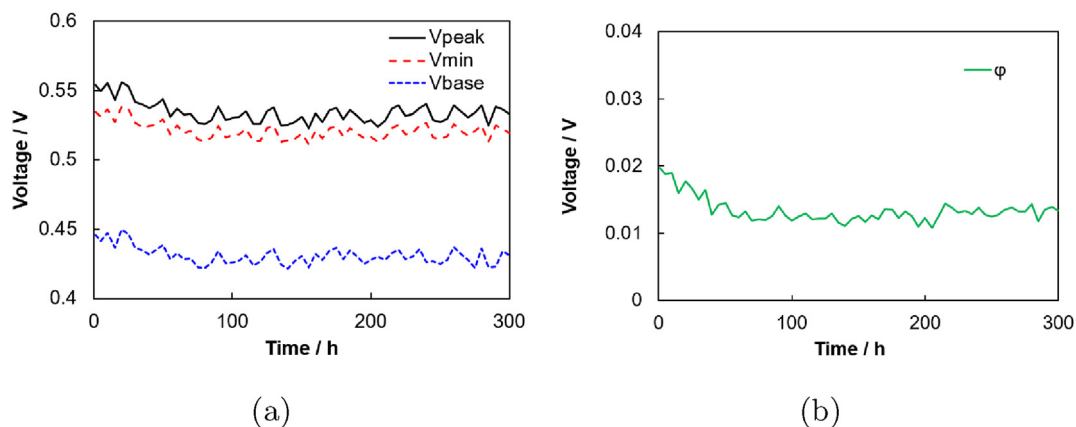


Fig. 4 – (a) Characteristic voltages (as described in [Fig. 1](#)) corresponding to V_{peak} (black), V_{min} (red), V_{base} (blue) and (b) overshoot φ (green) for JM MEA at 0.7 M MeOH and 60 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

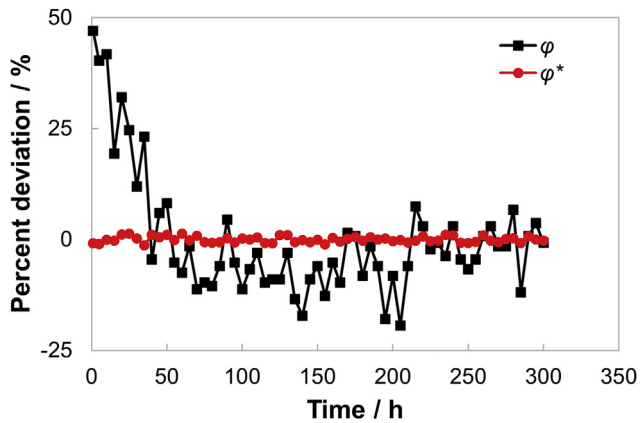


Fig. 5 – Comparison of the percent deviation of φ and φ^* calculated according to Eq. (1) for JM MEA.

This φ^* is even more beneficial when the cell is operated at different temperatures. The temperature of a DMFC system during the operation can fluctuate by as much as ± 5 °C [33].

Fig. 6a and c shows the overshoot behaviour for two different MEA types, Solvicore and JM MEA, respectively. φ magnitude at a given concentration increases with temperature. This indicates the need for a temperature dependent calibration of every MEA. However when φ is processed

according to Eq. (1), the temperature effects for both MEAs are nullified, as shown in Fig. 6b (Solvicore MEA) and 6d (JM MEA). In certain conditions, e.g. when the original overshoot was negative at 0.4 M for JM MEA, the corresponding φ^* did not produce a satisfying result but the accuracy was still maintained better than ± 0.1 M. The range of φ^* for all concentrations (0.4 M–0.8 M) for Solvicore and JM MEA is 0.135 V to 0.114 V and 0.165 V to 0.111 V, respectively. This range mainly differs due to the φ^* values of JM MEA at 0.4 M. Note the similarities between the φ^* values at 0.5, 0.6, 0.7 and 0.8 M for JM and Solvicore MEA despite strong difference in their performance at given methanol concentration as shown in Fig. S1. This striking result shows that φ^* remains unaffected even when different MEAs are used. Therefore, the applied processing of the overshoot was also used to analyse the stack results.

Stack

When the formula for a single cell is adapted to the stack level, few main differences should be considered. The system layout, including the recirculation loop of methanol solution in Fig. 1, differs from the open loop system of the single cell test layout, which means that other species, such as nitrogen or formic acid may accumulate in the loop and disturb the sensitive measurement due to interaction at the Pt surface. The active area of each cell in the stack is eighteen times

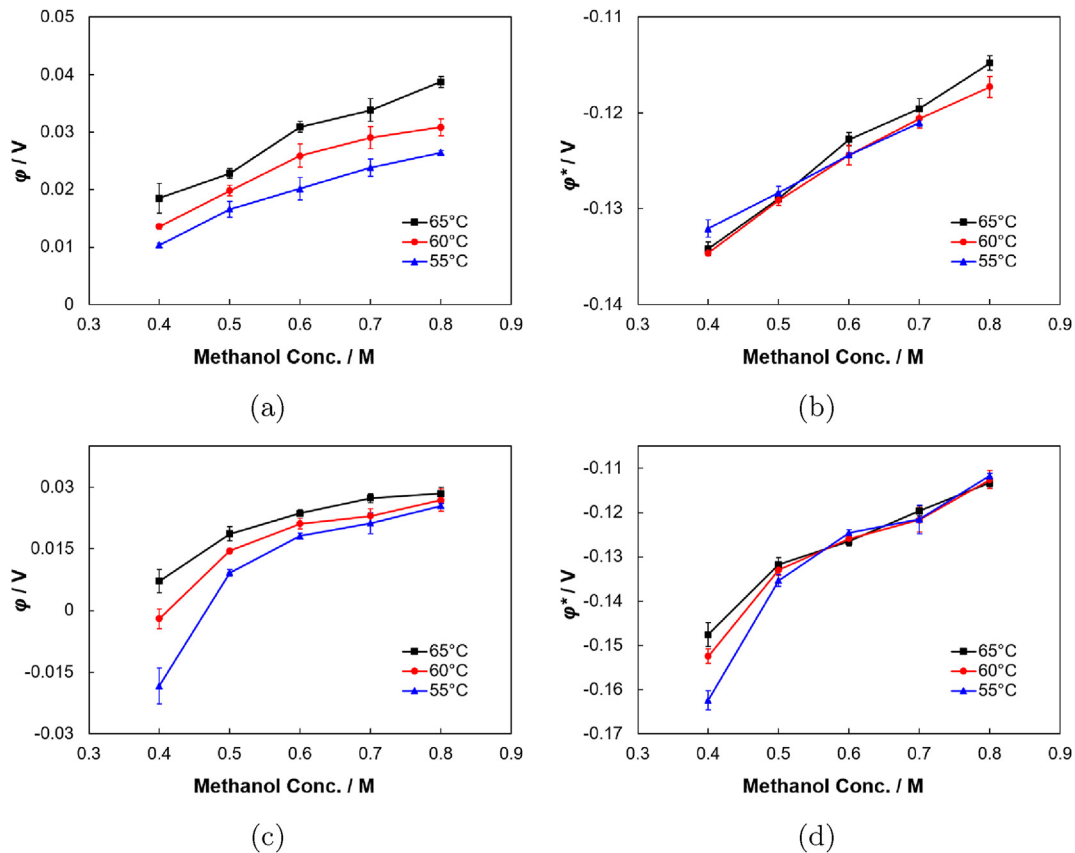


Fig. 6 – φ and φ^* behaviour with respect to the methanol concentration at 65 °C (black), 60 °C (red) and 55 °C (blue). (a) $\varphi_{1.8}$ of Solvicore MEA (b) φ^* of Solvicore MEA (c) φ of JM MEA (d) φ^* of the JM MEA. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

larger than that of the single cell. With the large active area, the reactants concentration at the catalyst layer stabilizes more slowly than in the single cell. Therefore, the overshoot voltage stabilized after 3.0 s instead of 1.8 s in the single cell. The stack has an overshoot value for each cell and therefore average of φ and φ^* must be considered. Hence Eq. (1) for stack is modified as follows:

$$\varphi_{avg}^* = \varphi_{avg} \frac{V_{peak,avg}}{3.75} \quad (2)$$

Note that the same fraction, 1/3.75, was used as for the single cell, Eq. (1). This relation proved robust. Furthermore, the voltages of the five cells in the stack were measured at the same time. Due to different temperature and flow conditions with a stack, it is expectable that voltage signals deviate and that some cells show outliers. To account for this effect, we discarded the cells with the largest and the smallest voltage and averaged the remaining three signals. Similar to the single cell, the φ_{avg} is significantly influenced by the operating temperature, as is shown in Fig. 7a. However, the φ_{avg}^* again shows a temperature independent correlation of signal and concentration (Fig. 7b). From the 92 measurements of the overshoot values, all concentration measurements were within ± 0.1 M, which fulfils the criterion for usage for system operation.

To derive a trend curve with which directly the concentration can be estimated, the φ_{avg}^* is entered in the following empirical equation, where C_{est} is the estimated concentration:

$$C_{est}(\varphi_{avg}^*) = e^{\frac{\varphi_{avg}^* + 0.1147}{0.0308}} \quad (3)$$

As visible in Fig. 7b, the trend curve reproduces the dependence of concentration on the modified overshoot well. Hence irrespective of the stack operating temperature, the algorithm for concentration detection requires only two inputs V_{peak} and V_{min} . From the V_{peak} and V_{min} determined at the given time period of the stack operation, for instance V_{peak} and V_{min} determined in step 3 of Table 1, the methanol concentration can be estimated by Eq. (3). No additional input of temperature, methanol flow rate, air flow rate or degradation rate is required to estimate the methanol concentration simplifying the sensing technique to a great extent.

Finally, the overshooting based concentration estimation technique is validated at stack level in a closed loop configuration which resembles a typical system operation. When the target concentration changed between 0.4 M and 0.8 M intentionally to maximize fuel cell efficiency, the methanol solution is measured by the refractometer and calculated. The long term measurement over several hours is compared with concentration measurements with a refractometer. The refractometer is used instead of a density meter to avoid noise signal from the bubble trapping. The results are displayed in Fig. 8. Both concentration measurement techniques show the same temporal evolution of concentration during the measurement. The offset visible between the estimated concentration and the measured concentration by the refractometer can result from the biased sensor because the refractometer has a long line tube for online measurement. Temperature difference, in the long line tube at the lab scale open loop system, can result in a biased measurement, while the compact density meter is equipped with the short tube in actual systems. Even if the same MEA was used in the stack as in the single cell, the locally different electrochemical reactions averaging in the larger active area of the stack can bias the electrochemical response within 4.97% from the reference of the single cell based equation. It can be concluded that the presented concentration sensing technique based on voltage dynamics indeed is able to predict concentration very well during a long term measurement and for various levels and systems and uncertainties due to operating conditions and degradation.

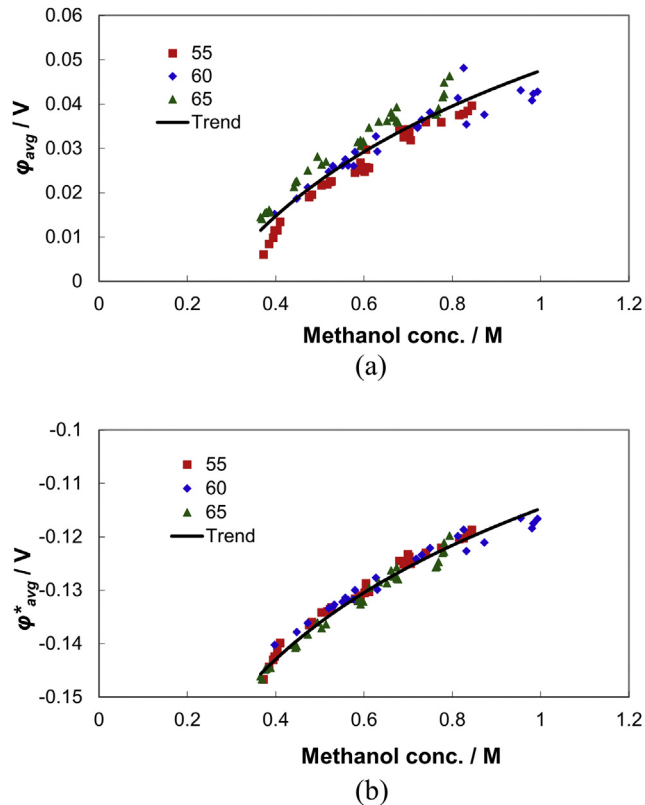


Fig. 7 – (a) Overshoots, φ_{avg} , and (b) modified overshoots, φ_{avg}^* vs. the methanol concentration of the stack in a closed loop system at 55 °C, 60 °C and 65 °C.

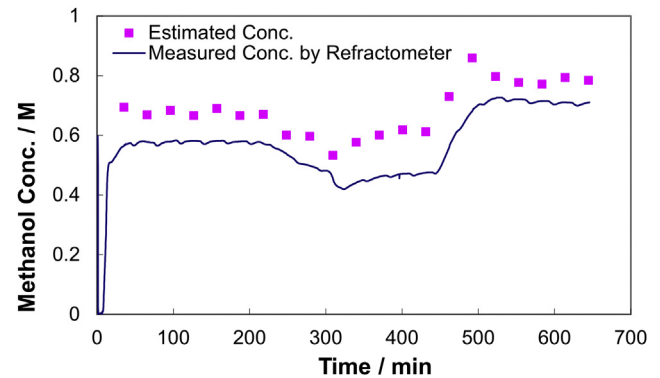


Fig. 8 – Validation of the concentration estimation method with a refractometer for 10 h in the closed system at stack level.

Conclusions

The dynamic behaviour of the DMFC, notably the overshooting voltage response to a step change in current, was found to be sensitive to the methanol concentration and was exploited to estimate the concentration of the methanol in the stream entering the fuel cell. The robustness and accuracy of the sensing method improved significantly when we also took the peak voltage of the overshoot into account, apart from its magnitude. An empirical equation that is a function of only overshoot magnitude and overshoot peak potential was able to nullify the effect of the MEAs, cell degradation and temperature even when the temperature changed by 10 °C. This improved the sensing accuracy to better than ± 0.1 M and massively reduced the number of experiments required to create the reference database. The same correlation between concentration and overshoot was also validated in a 5 cell stack operating in the open and closed loop configuration. In the stack, the overshoot containing equation could nullify the effect of the cell degradation and temperature. Hence in this work we showed that a methanol estimation technique based the dynamic voltage signal according to the overshooting principle is reliable and accurate up to ± 0.1 M and can be used in DMFC systems or for other methanol sensing purposes.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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