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Extended criterion for robustness evaluations of energy conversion efficiency in DMFCs

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ABSTRACT

Considering the effects of unpredictable disturbances, a robustness criterion is newly proposed to develop an integrated evaluation with modified efficiency criterion, for comprehensive assessments of energy conversion performances in direct methanol fuel cells. The effectiveness of developed criteria in various situations (including some extreme operating conditions) has been carefully analyzed based on both experimental and numerical results. For undisturbed operations, the modified efficiency criterion could help to avoid potential misinterpretations of energy conversion process in existing criteria. For disturbed operations, the robustness criterion concerning the effects of uncertainty propagations is shown to be an effective guidance for the determination of appropriate operating current densities to design efficiency-stabilized operations. Systematic analysis on its applications in different situations proves that, the integrated efficiency and robustness evaluations can effectively differentiate the effects of operating conditions and membrane types, which is highly beneficial for one's optimal designs of stable and efficient DMFC operations.

1. Introduction

Direct Methanol Fuel Cell (DMFC) is regarded as a prosperous power source for mobile applications attributing to its features of easy handling, rapid charge and high energy density, etc. [1,2]. Lots of efforts have been carried out to improve the DMFC performance for accelerating its commercialization during the past decades [3], such as the optimization of cell structure [4], the improvement of catalyst loading [5] and the amelioration of fuel delivery system [6]. In one's evaluations of those performance-enhanced techniques, how to determine an effective criterion for DMFC operations can be an important problem and therefore deserves further discussions [7,8].

A widely applied assessment of DMFC performance is the relationship of current density (I) and voltage (V) or power density (P), i.e., I-V or I-P curves. Coming very naturally from their definitions, the polarization effects and the output characteristics of DMFC systems can be well depicted [9,10]. However, the I-V and I-P curves mainly concentrate on the system output, rather than the energy conversion process. Under different hypotheses, several criteria were proposed to assess the energy conversion efficiency during the past decade [11,12]. One of the main criteria considers the fact that the energy conversion efficiency is highly relevant with the fuel waste (i.e., methanol crossover effect). It utilized a single-parameter index, the effectiveness of fuel utilization (the ratio between the power-generated fuel amount and the overall fuel consumption), to measure the energy conversion efficiency [11,12]. However, the output characteristics has not been taken into account. Considering the polarization effect, a double-parameter index was proposed to evaluate the overall efficiency by multiplying the potential and Faraday/current efficiencies [13,14]. A very similar criterion was also deduced from the ratio between the output power density and the low heating value of overall fuel consumption [15]. Another type of criterion that was designed to concern about more systematical effects is the triple-parameter index, in which the total efficiency was considered by a product of several parameters accounting for fuel consumption, thermodynamic and voltaic efficiencies [16–18]. Such systematic considerations for global efficiency were also applied to evaluate the DMFC system only at its largest power output [19].

In spite of huge progress has been made, most of the existing criteria have been confined to evaluate DMFC systems with stable operating conditions. However, the environmental disturbances, e.g., the noise of operating parameters or the small variations in load conditions [20,21],

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Nomenclature

ΔG	change in Gibbs free energy
ΔH	enthalpy change in Gibbs free energy
η	energy conversion efficiency
η_F	Faraday efficiency
η_{mod}	system efficiency at undisturbed conditions
η_P	potential efficiency
η_T	thermodynamic efficiency
$\bar{g}$	gibbs free energy in one mole of methanol
C_M	methanol concentration
F	Faraday constant
F_A	air flow rate
F_M	methanol flow rate
F_{MeOHin}	input methanol amount
$F_{MeOHout}$	output methanol amount
F_{MOR}	effective methanol consumption
I	operating current
I_{cross}	crossover current
LHV	lower heating value
N_{cons}	molar flow rate of methanol for effective current generation
N_{cross}	molar flow rate of methanol crossover
R	robustness
T	temperature
V_{cell}	operating voltage
V_{th}	thermodynamic reversible voltage

need to be taken into account in the criteria development for a comprehensive evaluation of the energy conversion performance in DMFCs [22–25]. Systematic robustness has been widely applied to evaluate the ability of a system to resist environmental disturbance without adapting its initial stable configurations in the design, analysis and improvement of energy systems [24,26,27]. For instance, the robustness analysis has been successfully applied to identify the effect of assembly parameters on the pressure distribution inside a stack of proton exchange membrane fuel cells [28]. A robust controller was developed with the consideration of operating condition variations to improve the power output of fuel cells for automotive applications [29]. Robustness analysis has also played an important role in the development of fault diagnosis method for air-feed fuel cell systems [30]. However, to the best of our knowledge, the systematic robustness is not yet applied in the evaluations of DMFC performance in spite of its high potential, which then becomes the initial motivation of the present study.

Considering the effects of unpredictable disturbances, a robustness criterion is creatively proposed to develop an integrated evaluation with modified efficiency criterion. This integrated evaluations can be applied to comprehensively assess the energy conversion performances in DMFC systems. Methodologies are presented in Section 2, where the efficiency and robustness criteria, as well as the applied numerical and experimental techniques, are all detailedly elaborated. Comparative study between the existing and modified efficiency criteria is firstly presented (Section 3.1), and the applications of efficiency evaluations on disturbed operations are subsequently investigated to study the necessity of robustness evaluations Sections 3.2 and 3.3. Applications of integrated efficiency and robustness evaluation in various situations (including some extreme operating conditions) are then performed and carefully discussed in Section 3.4. Conclusions are summarized in Section 4.

2. Materials and methods

Systematic analysis on the efficiency and extended robustness evaluations in DMFC systems is performed based on the collaborations of experimental and numerical techniques. In this section, the applied experimental and numerical techniques, as well as the evaluation criteria are described. Firstly, the experimental platform is presented, and then some preliminary experimental works based on DMFCs with different Membrane Electrolyte Assemblies (MEAs) are carried out to generate reference data for numerical validations. Numerical models about the energy conversion process inside DMFCs are then validated and presented. Subsequently, the existing classical criteria of efficiency evaluations are comprehensively described, and thereafter, a newly modified efficiency criteria as well as the extended robustness evaluation are both proposed in details.

2.1. Experimental setup

Fig. 1 shows the experimental set-up of DMFC testing system. The peristaltic pump (BT300LC) is used to transport the methanol solution composed by deionized water and pure methanol, while an air compressor (OUTSTANDING OTS-550) regulated by a mass flow controller (OMEGA FMA-2605A) is applied to pump the air into the cathode side. A supplementary heating apparatus controlled by a temperature controller (Omega CSC32) is used to regulate the operating temperature. During operations, the DMFC performance is monitored by an electrochemical workstation (CHI660E), and the production of CO_2 is measured by a CO_2 concentration detector (JA500-CO2-IR1). The current density is regulated by an electronic load device (ITECH it8211) to different levels, and the corresponding voltage is thus measured.

Several DMFCs with different MEAs have been applied in experiments for different research purposes (Fig. 1, bottom). In order to study the effects of operating conditions, a specific single-cell DMFC consisting of a five-layer MEA with an effective active area of $25\,cm^2$ sandwiched by graphite end plates with serpentine channels of 30 passes. The five-layer MEA is composed by a Nafion 212 membrane, an anode catalyst layer with $4.0\,mg/cm^2$ Pt loading, a cathode catalyst layer with $0.03\,mg/cm^2$ Pt loading and two gas diffusion layers. Besides, the effects of membrane types are also investigated by introducing Nafion 115 and 117 membranes, for which the catalyst loading and active area are kept to be the same with those of Nafion 212. It is important to notice that the thicknesses of Nafion 115, 117 and 212 membranes are 127, 183 and 50.8 μm, respectively.

2.2. Numerical model

Considering the integrations of the governing equations of continuity, momentum conservation, species transport and electrochemical phenomena, we have developed a three-dimensional numerical model to investigate the energy conversion process in DMFC systems [31]. The overpotential effects including concentration, activation and ohmic ones are accounted by a semi-empirical model which has been well embedded inside this numerical model. It has shown a good agreement with experimental results in our previous studies, and has been successfully applied to study the underlying mechanisms of energy conversion process, the combined effects of different operating parameters and the operation strategy to enhance the voltage stability in different DMFC systems [31,32]. We have applied this well-constructed numerical model in the present study. For simplicity and concision, more details are not contained here but can be available in Refs. [31,32].

Numerical simulations were performed using a Computational Fluid Dynamics (CFD) code known as Fluent 16.0 which is based on the finite volume method. The manually defined parameters/conditions are all coded by User Defined Functions (UDFs) and then integrated into the CFD model. Flow domains are discretized into structured grids,

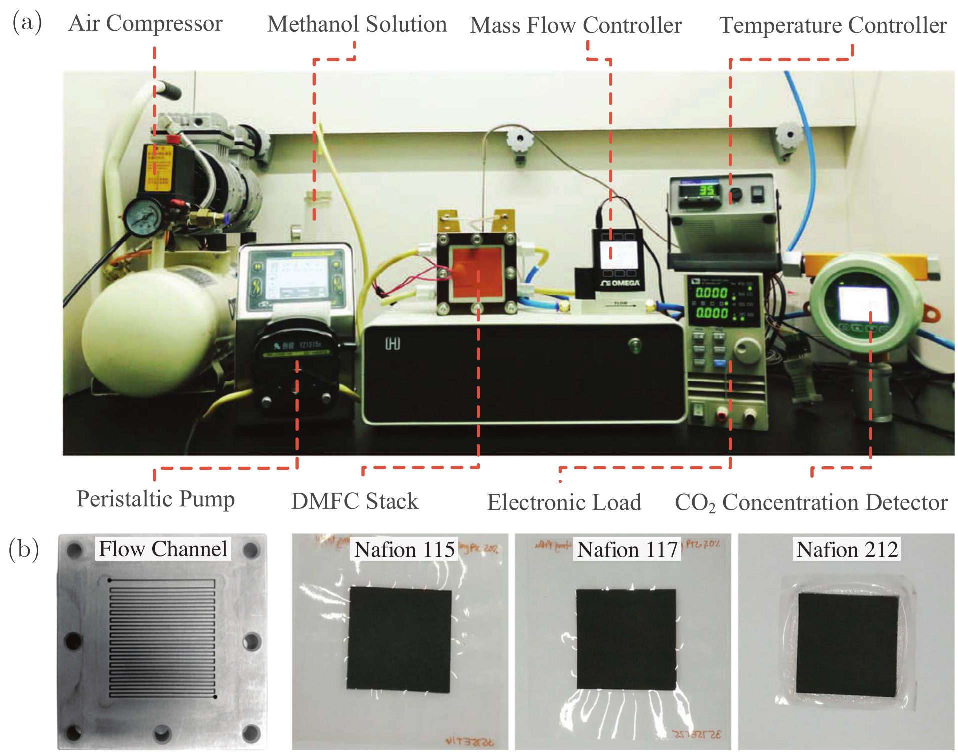

Fig. 1. Experimental set-up of direct methanol fuel cell system. (a) Testing system. (b) Flow channel configuration and MEAs with different Nafion membranes.

consisting of 416240 cells and 522900 nodes. No-slip conditions are employed for all boundary walls. The conditions of velocity inlet and pressure outlet are defined at the inlet and outlet of flow channel. The other operating parameters, such as methanol concentration and operating temperature, are defined according to experimental conditions at corresponding regions. The governing equations of incompressible flows are solved by the implicit and pressure-based solver, while the pressure-velocity coupling process is achieved by SIMPLE algorithm. We consider a numerical simulation to be steady, when a stable value of current density is achieved through sufficient iterations.

For validations, the I-V curves obtained from numerical simulations are compared to experimental results (Fig. 2). The numerical predications coincide very well with experimental data, which shows the reliability and feasibility of constructed models. Plenty of simulations are then performed to study the energy conversion process in DMFC

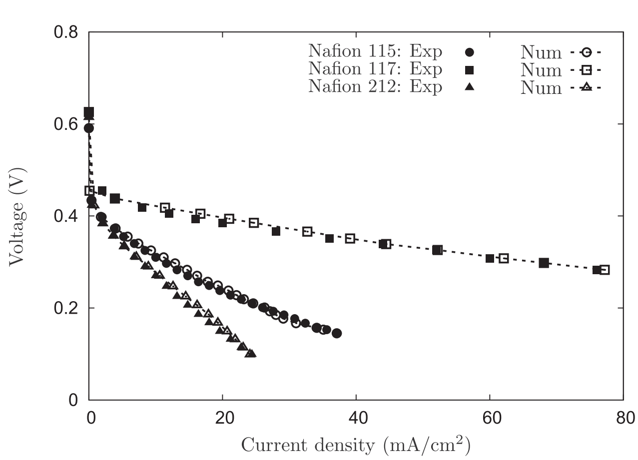

Fig. 2. Comparisons of experimental and numerical I-V curves. Operation condition is maintained at the stable state of temperature T= 348.2 K, input methanol concentration C_M = 1.00 M, input flow rates of the feed solution F_M = 1.50 ccm and the air F_A = 200 ccm.

systems at different operating conditions.

2.3. Evaluation criteria

A large number of criteria have been developed to evaluate the energy conversion efficiency of DMFCs during the past decades. A representative type assumes the energy conversion efficiency is directly determined by the effectiveness of fuel utilization [11,12]. It is classified as single-parameter index in present study, which takes a similar form as follows,

$$\eta = \frac{F_{MOR}}{F_{MeOHin} - F_{MeOHout}}, \quad F_{MOR} = \frac{I}{6F}, \tag{1}$$

where η is the energy conversion efficiency, F_{MOR} is the effective methanol consumption for current generation, and F_{MeOHin} and $F_{MeOHout}$ are the input and output amounts of methanol, respectively. Effective methanol consumption F_{MOR} can be determined from the operating current I and the Faraday constant F, as presented above. And the difference between F_{MeOHin} and $F_{MeOHout}$ denotes the actual fuel consumption, which actually consists of the effective methanol consumption F_{MOR} and the methanol crossover (i.e., fuel waste).

A type of double-parameter index was also proposed by multiplying the Faraday and potential efficiencies with special consideration of non-negligible output characteristics (or polarization effect) in efficiency evaluations [13,14]. It takes a typical form as,

$$\eta = \eta_F \times \eta_P = \frac{I}{I + I_{cross}} \times \frac{V_{cell}}{V_{th}}, \tag{2}$$

where the Faraday efficiency η_F is calculated by a function of operating current I and crossover current I_{cross}, and the potential efficiency η_P equals to the ratio between operating voltage V_{cell} and thermodynamic reversible voltage V_{th}.

Concerning about more systematical effects, another type was defined to evaluate the total efficiency by the means of integrating the Faraday, potential and reversible thermodynamic efficiencies [16–19]. The typical formation for this so-called triple-parameter index is as,

$$\eta = \eta_F \times \eta_P \times \eta_T = \frac{I}{I + I_{cross}} \times \frac{V_{cell}}{V_{th}} \times \frac{\Delta G}{\Delta H}, \tag{3}$$

where η_T denotes the thermodynamic efficiency. It can be derived from the ratio between the change in Gibbs free energy ΔG and the enthalpy change ΔH.

It is also of importance to notice that, Casalegno et al. have proposed a concise criterion with a very similar assumption to that of double-parameter index [15]:

$$\eta = \frac{V_{cell} I}{LHV\,(N_{cons} + N_{cross})}, \tag{4}$$

where LHV is the lower heating value of methanol, N_{cons} and N_{cross} denote the molar flow rates of methanol for effective current generation and the methanol crossover, respectively. Compared with the other criteria considering that the full efficiency is integrated by several subparts, this criterion depicts the energy conversion process from a global perspective of the whole DMFC systems. It evaluates the full efficiency by the ratio between electrical power output and chemical energy input per unit time. It is, apparently, with more explicit physical meaning and also easy to implement. Nevertheless, as LHV is inherently inextricable from fuel combustion process, its utilization may misinterpret the intensity of energy conversion process in DMFC systems in which the combustion phenomenon does not objectively exist. In view of this, we propose to use Gibbs free energy per mole $\bar{g}$ to substitute LHV in Eq. (4). A newly modified criterion η_{mod} is then expressed as,

$$\eta_{mod} = \frac{V_{cell} I}{\bar{g}\,(N_{cons} + N_{cross})}. \tag{5}$$

Plenty of applications have shown the feasibility of those efficiency criteria, however, most of them are confined to the assessments of energy conversion process at theoretically steady states. As system disturbance is normally inevitable, the system ability to resist external disturbance needs to be taken into account in one's evaluations of DMFC performance. Therefore, we propose to apply the robustness analysis on energy conversion efficiency in DMFCs. Following the modified Taguchi method [33,34], the extended criterion for robustness analysis is defined based on the modified efficiency criterion Eq. (5). It can be expresses as,

$$R = \frac{\eta_{mod}}{\Delta\eta_{mod}}, \quad \Delta\eta_{mod} = \left| \frac{(V_{cell} + \Delta V_{cell}) I}{\bar{g}\,(N_{cons} + \Delta N_{cons} + N_{cross} + \Delta N_{cross})} - \eta_{mod} \right|, \tag{6}$$

where R denotes the robustness that can be regarded as 'signal-to-noise' ratio in modified Taguchi method. η_{mod} is the system efficiency under undisturbed condition (considered as 'signal'), while $\Delta\eta_{mod}$ is the deviation of system efficiency from its undisturbed conditions caused by environmental disturbance (considered as 'noise'). ΔV_{cell}, ΔN_{cons} and ΔN_{cross} represent the changes in operating voltage, molar flow rates for effective methanol consumption and methanol crossover, respectively. It is of importance to notice that, the robustness Eq. (6) are suggested to be utilized collaboratively with the criteria of energy conversion efficiency Eq. (5), to achieve comprehensive evaluations of energy conversion process of DMFC systems.

3. Results and discussions

3.1. Efficiency evaluations

Comparative study of low-efficiency evaluations could help to differentiate the characteristics of different criteria. Nafion 212 membrane is thus considered in this section, attributing to its comparatively small thickness of 50.8 μm which could lead to high methanol crossover and low energy conversion efficiency in DMFCs [35,36]. Numerical model that has been validated by experimental data is applied to simulate the energy conversion process with operating conditions of the working temperature $T = 309.0$ K, the methanol concentration $C_M = 0.75$ M, the methanol flow rate $F_M = 4.55$ ccm and the air flow rate $F_A = 800$ ccm. Numerical results are subsequently used for efficiency evaluations by different criteria.

Fig. 3(a) shows the energy conversion efficiencies evaluated by existing criteria. For single-parameter indexes (Eq. (1)) [11,12], the energy conversion efficiency is observed to grow consistently with current density. As the single-parameter index represents the ratio of effective fuel consumption to total fuel investment (Eq. (1)), this result coincides with the common phenomenon that a higher current generation normally requires more effective fuel consumption. However, it is well-known that the increase of current density is normally accompanied by aggravation of energy loss, resulting from the accumulating inner resistance consumption [8,37]. This physical fact, also known as ohmic polarization effect, has been neglected in single-parameter index.

Polarization effects have been taken into account in double-parameter indexes by introducing one new term for potential efficiency (Eqs. (2) and (4)) [13–15]. As shown in Fig. 3(a), the efficiency evaluated by double-parameter indexes is found to increase with current density at the low current density region, and it turns to decline when the peak value is reached at 8.6 mA/cm². Such tendency is supposed to come from the coupling effects of methanol crossover and ohmic loss. More specifically, a low current density (i.e., low current generation) normally implies a large proportion of unconsumed methanol in feed solution [37], which could aggravate the methanol crossover effect and rightfully lead to considerable fuel waste. As current density grows, the proportion of consumed methanol in feed solution rises [15], and the

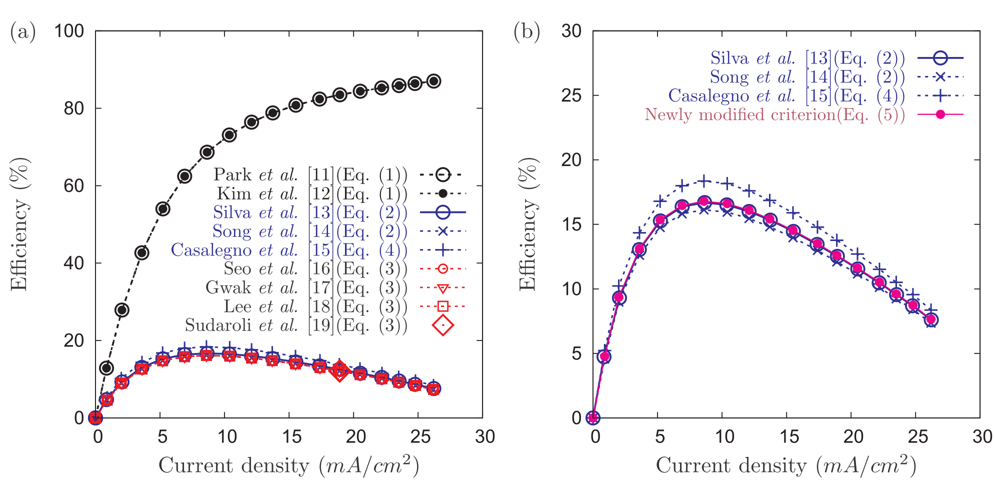

Fig. 3. Evaluations of energy conversion efficiency using existing criteria (a) and newly modified criterion (b). Color is applied to differentiate the index types.

consequent shrinkage in methanol crossover makes the energy conversion efficiency to increase. However, the effect of ohmic loss, which could restrain the energy conversion efficiency, can be also exaggerated with the increase of current density [8,37]. A dominating effect of ohmic loss could be the reason for downward trend of energy conversion efficiency in the high current density region ($\geqslant 8.6\,mA/cm^2$). As the tendency of energy conversion efficiencies conforms to physical facts and logical predications, the reasonability of double-parameter index could have been explained to some extent.

Compared with double-parameter index, the triple-parameter one (Eq. (3)) [16–19] introduces one additional term to consider reversible thermodynamic efficiency. However, as the approximation of this additional term is usually close to about 97% (e.g., 96.7% in [38] and 97.0% in [39]), the difference between the double- and triple-parameter evaluations is not notable in Fig. 3(a). Such a good agreement has further confirmed the effectiveness and reliability of the double-parameter index. It is also of interest to notice in Fig. 3(a) that the single point represents a specific utilization of triple-parameter index, i.e., to generally evaluate the system efficiency in the condition of the maximum power output [19].

In summary, the efficiency evaluated by the single-parameter indexes could be aggravated especially in the region of high current density, because of their negligence of polarization effects. Comparatively, the double-parameter indexes, that consider the polarization effects using the supplementary potential efficiency, could provide more physically meaningful predications in system efficiency. Moreover, the triple-parameter indexes introduce one additional term to consider reversible thermodynamic efficiency. However, their predications still coincide very well with those of double-parameter indexes, as the approximation of reversible thermodynamic efficiency term is usually close to about 97.0%. It implies that the double-parameter index could be preferable in practical applications owing to its simplicity in calculations.

Fig. 3(b) shows the comparisons of efficiencies evaluated by the classical double-parameter index and the newly modified criterion. Our modified efficiency criterion (Eq. (5)) predicts the system efficiency to increase with current density, and then turn to decline when a peak value of 16.79% is reached at $8.6\,mA/cm^2$. This tendency matches well with that of classical double-parameter indexes, which could validate the reasonability of the newly modified model to some extent. However, a slight difference can also be noticed. It lies in the fact that the LHV in concise double-parameter criterion (Eq. (4)) is substituted by Gibbs free energy in the modified criterion (Eq. (5)). As LHV is originally defined in combustion process, it would overestimate the energy conversion efficiency in DMFCs. Such a misinterpretation of energy conversion process can be avoided by the using of Gibbs free energy in the modified criterion. As it can provide reasonable results with clear physical meanings, the newly modified criterion is therefore adopted in the following evaluations.

3.2. Effect of environmental disturbance

Operational uncertainty, caused by environmental disturbances such as mechanical vibration and temperature fluctuation, is usually unpredictable in practical DMFC applications [24,32]. Energy conversion performance of DMFCs is thus inevitably affected by those operational uncertainties. Such effect of uncertainty propagations has received relatively less attention in previous studies about DMFC system evaluations, even if the energy conversion efficiency of stable operations can be well estimated using existing criteria (see Section 3.1). This problem is then concerned in this section by experimental techniques.

Four main operating parameters are considered in our experiments, i.e., the methanol concentration (C_M), the working temperature (T), the flow rates of feed methanol solution (F_M) and air (F_A) [10,31]. Since methanol concentration (C_M) is comparably stable in practical applications and the DMFC performance is insensitive to the disturbances in air flow rate (F_A), they are considered to be stable in our experimental design. The main concerns in our experiments are thus the effects of operational uncertainties in working temperature (T) and methanol flow rate (F_M). Experimental study is designed to compare different system responses under undisturbed and disturbed operations.

Table 1
Disturbed operating parameters and its deviation in uniform-designed experiments.

No.	T (K)	Deviation of T	F_M (ccm)	Deviation of F_M
1	299.1	−2.95%	4.54	0.89%
2	302.4	−2.20%	4.45	−1.11%
3	304.5	−1.18%	4.50	0%
4	305.3	−0.92%	4.49	−0.22%
5	306.2	−0.63%	4.39	−2.44%
6	307.3	−0.27%	4.45	−1.11%
7	309.0	0.27%	4.54	0.89%
8	309.9	0.57%	4.52	0.44%
9	310.9	0.90%	4.59	2.00%
10	313.0	1.56%	4.52	0.44%

For undisturbed operation, the operating parameters are set as $C_M = 0.75$ M, $F_A = 800$ ccm, $T = 308.15$ K and $F_M = 4.5$ ccm, which are selected to achieve moderate energy conversion process based on experimental experience [10,31,32]. For disturbed operations, a small variation is intentionally imported in working temperature (T) or/and methanol flow rate (F_M), to account for operational disturbances that might be encountered in practical applications. More specifically, the operational disturbances are assumed to follow nominal distributions around the undisturbed values, ten levels are selected according to random selection in the nominal distributions. Experimental design is then based on the uniform design principle [40], and ten experimental tests are designed and performed (Table 1). Experiments are performed based on the single-cell DMFC with Nafion 212 membrane. Energy conversion efficiency of undisturbed and disturbed operations are subsequently evaluated using the newly modified criterion (Eq. (5)).

Fig. 4 shows the evaluated efficiencies of undisturbed and disturbed operations. For undisturbed operation, the energy conversion efficiency continues to increase with current density, until a peak value of 7.74% is achieved at the current density $5.2\,mA/cm^2$. It then turns to decrease to a relatively low value of 3.76% at $18.0\,mA/cm^2$. The efficiency evaluation coincides well with physical predications (as discussed in Section 3.1), which confirms again the feasibility of newly modified efficiency criterion for stable operations.

For disturbed operations, the evaluated efficiencies are found to fluctuate near the undisturbed results (dot plots in Fig. 4). For instance, the disturbed efficiency varies from 4.51% to 8.35% at $5.2\,mA/cm^2$, at

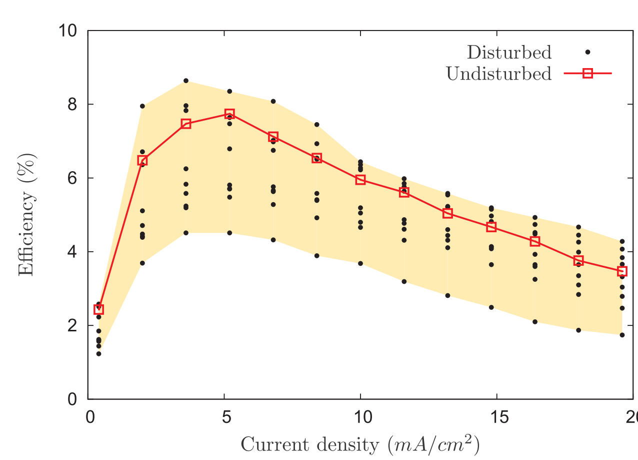

Fig. 4. Efficiency evaluations of disturbed and undisturbed DMFC operations. Shadow area is used to denote the distribution region of disturbed results.

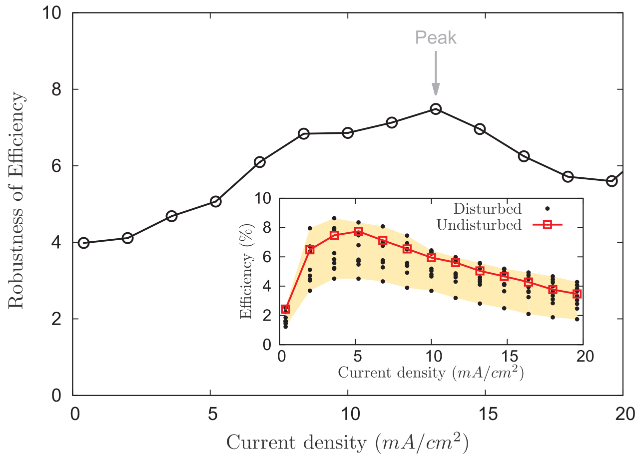

Fig. 5. Robustness analysis of energy conversion efficiency on experimental results. Miniature of Fig. 4 is arranged at the right corner for comparisons.

which the undisturbed efficiency achieves its peak value of 7.74%. The deviation between disturbed and undisturbed results is from −41.73% to 7.88%. However, the deviations of working temperature (T) and methanol flow rate (F_M) from undisturbed states are both less than 3% (Table 1). Such a small operational disturbance is supposed to make a small fluctuation, other than the presented large variations in efficiency evaluations [17,24,41]. This unexpected result reminds us that, the efficiency evaluation could not be comprehensive for one's assessment of energy conversion performance in DMFCs, for which the proposed robustness criterion (Eq. (6)) would be beneficial. Moreover, the operating current density for maximum efficiency is found to be different in disturbed and undisturbed operations (Fig. 4). Specifically, it is at current density 5.2 mA/cm^2 for undisturbed operation, but at 3.6 mA/cm^2 for disturbed operations. Such an unidentifiable system characteristics using efficiency evaluation once again reminds us that, the robustness evaluation could be necessary for comprehensive assessment in DMFCs, especially when the effects of uncertainty propagation are non-ignorable.

3.3. Extended robustness evaluations

Energy conversion performance of disturbed operations is then analyzed using the extended robustness criterion (Eq. (6)). For comparisons, the robustness evaluations are also based on the same experimental data in Section 3.2. Evaluated robustness of system efficiencies is shown in Fig. 5. It is found to grow rapidly from 4.0 to 6.8, as the current density increases from 0.4 to 8.4 mA/cm^2. After that, the increment speed turns to be relatively low, i.e., it grows slowly from 6.8 to 7.5 as the current density varies from 8.4 to 13.2 mA/cm^2. A sharp decrease can be observed after the peak value of 7.5 at 13.2 mA/cm^2. Since the extended robustness criterion is defined to assess the system ability to resist operational disturbances, it implies that the DMFC system can be more stable to be operated in the current density range of [8.4, 13.2] mA/cm^2. The extended robustness evaluation has provided a guidance to determine the appropriate current density for stable operations.

It is still full of interest to notice in Fig. 5 that the highest robustness occurs at 13.2 mA/cm^2, but the maximum efficiency occurs at 3.6 mA/cm^2 for undisturbed operations. It suggests that the maximum efficiency and the highest robustness (or stability) cannot be guaranteed simultaneously, and the energy conversion performance should be assessed using the integrated efficiency and robustness evaluations. However, this preliminary conclusion is deduced based on a specific DMFC system. Further studies are still needed to validate the integrated efficiency and robustness evaluations to various conditions (e.g., different operating conditions and MEA membranes).

Table 2
Different operating conditions at undisturbed states.

Case	T (K)	C_M (M)	F_M (ccm)	F_A (ccm)
I	308.2	0.75	0.50	400
II	318.2	1.50	1.50	1000
III	348.2	1.00	1.50	200
IV	328.2	0.50	2.50	600
V	308.2	0.75	4.50	800

3.4. Integrated efficiency and robustness evaluations

Systematic analysis is carried out to study the feasibility and effectiveness of integrated efficiency and robustness evaluations in various DMFC operations. For comprehensive validations, plenties of numerical simulations are performed to provide the data pool of DMFC operations with different operating conditions and MEA membranes. And some supplementary experiments are also performed to serve as practical situations for the integrated efficiency and robustness evaluations. More details are included in the following content.

3.4.1. Applications to different operating conditions

DMFC performances at different operating conditions can be well predicated using numerical simulations [21,31,32]. In Section 2.2, our numerical model for energy conversion process in DMFCs has been validated by experimental results of different DMFCs. Concentrating on the DMFC with Nafion 212 membrane, numerical simulations are carried out to study the effects of operating conditions.

According to experimental experience, several groups of operating parameters are considered as typical undisturbed DMFC operations (Table 2). Disturbed operations which account for the effects of operational disturbances are designed based on the uniform design principle [40]. Specifically, the methanol concentration (C_M) and the air flow rate (F_A) are assumed to stay at the undisturbed values, while the operational disturbances occurring in working temperature (T) and methanol flow rate (F_M) are assumed to occur near the undisturbed values. Ten levels are selected for disturbed operating parameters according to random selection in nominal distributions, and ten numerical tests are designed for each of the five undisturbed operations. Altogether, more than 50 groups of numerical simulations are systematically performed for disturbed operations. Details about the operating parameters are summarized in Appendix, Table A.3. Numerical results are then adopted in the integrated efficiency and robustness evaluations.

Fig. 6(a) shows the evaluated efficiencies of undisturbed operations. Generally speaking, the efficiency variations for all the five cases show a fairly uniform tendency. It is found to increase at the region of low current density, but to decrease once the maximum efficiency is reached. Meanwhile, the evaluated efficiencies for different cases can be easily differentiated. For instance, the efficiency is larger for Case V than Case II at the range of low current density [0.3, 8.0] mA/cm^2, but the situation reverses when the current density exceeds 8.0 mA/cm^2. And the efficiency for Case I is always larger than the others in the whole range of operating current density. Moreover, the current density for maximum efficiency differs a lot with the operating conditions. For example, the maximum efficiency of 20.1% occurs at 5.6 mA/cm^2 for Case I, but it becomes 12.6% at 9.8 mA/cm^2 for Case III, and 13.1% at 8.0 mA/cm^2 for Case V. These results indicate that, the newly modified efficiency criterion could effectively differentiate the effects of operating parameters, which can be beneficial for one's development of optimized stable operations.

As shown in Fig. 6(b), diverse tendencies are found for the robustness evaluations of energy conversion efficiencies. For Case I, it increases rapidly at the low current density range ($\leqslant$ 7.0 mA/cm^2) and then stabilizes near 85.3 from 7.0 to 20.3 mA/cm^2. After that, it continues to grow up slightly to 125.2 at 23.0 mA/cm^2. In contrast, the

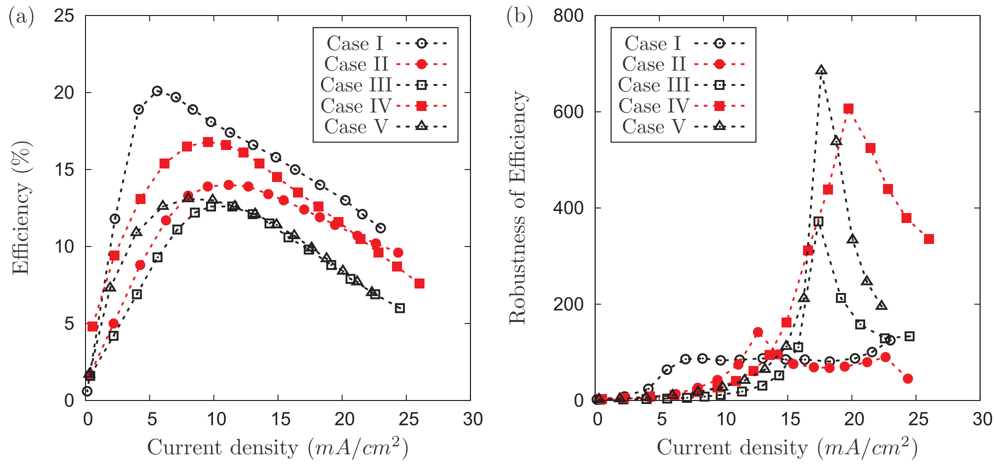

Fig. 6. Integrated efficiency and its extended robustness evaluations at different operating conditions.

robustness of Case III increases very slowly at the low current density range (⩽ 9.8 mA/cm²), and it increases with an accelerating rate until the highest value of 372.2 is reached at 17.4 mA/cm². It then shrinks rapidly to 129.3 at 22.6 mA/cm². A similar tendency can be also found for Case IV and V, but the operating current densities for the highest robustness is still diverse for different cases. Such distinguishable differences, not only in its variation tendency but also in the operating current density for the peak value, could be applied to differentiate the effects of operating conditions on the system abilities to resist operational disturbances.

Further deductions can be formulated from an integrated use of the efficiency and robustness evaluations. Among the five cases, the maximum efficiency is found to be provided by Case I in the whole range of current density (Fig. 6(a)). Not only that, the efficiency robustness for Case I is comparatively high at the low current density range ⩽ 10.0 mA/cm². It indicates that an optimal control for efficient and robust (or stable) DMFC operations in low current density range should be achieved in Case I. However, the efficiency robustness for Case I becomes relatively low at the high current density range (⩾ 10.0 mA/cm²), and the advantage of Case I in evaluated efficiency also becomes less notable especially compared to Case IV. It reminds us that the Case IV is better than Case I in the high current density range, which could provide considerable advantages in both operation efficiency and its stability. Such a comprehensive evaluation, that is deduced from the integrated use of efficiency and robustness criteria, can be highly beneficial for ones optimal design of DMFC operations.

3.4.2. Applications to different MEA membranes

Taking advantages of validated numerical models, systematic simulations are implemented to investigate the effects of membrane types (Nafion 115, 117 and 212) on the energy conversion performances. The undisturbed operations are designed as $T = 348.2$ K, $C_M = 1.00$ M, $F_M = 1.5$ ccm and $F_A = 200$ ccm, which are exactly the same as Case III in Section 3.4.1. For disturbed operations, the operational disturbances in working temperature (T) and methanol flow rate (F_M) are also kept the same as that of Case III in Table A.3, and more than 30 groups of numerical tests (10 for each MEAs) are systematically performed. Numerical results are then applied in the integrated efficiency and robustness evaluations.

Fig. 7(a) shows the efficiencies of stable operations in DMFCs with different membranes. The operating ranges of current density changes with the membrane type, which are [0, 77.2], [0, 36.6] and [0, 24.5] mA/cm² for Nafion 117, 115 and 212 membranes, respectively. At the low current density range (⩽ 9.8 mA/cm²), the efficiencies share a similar tendency of rapid increase for all the three membranes. It denotes that the effects of membrane types on efficiency could be ignorable when the current density is low. However, the maximum efficiency and the corresponding current density drastically change for different Nafion membranes, which are 26.4% at 44.5 mA/cm², 15.6% at 13.5 mA/cm² and 12.6% at 9.8 mA/cm² for Nafion 117, 115 and 212, respectively. It is also worthy to notice that the stabilized high-efficiency region is much wider for Nafion 117 than the others. More specifically, it stabilizes around a relatively high efficiency of 24.6% (with small fluctuation of ± 7.7%) from 16.7 to 77.2 mA/cm². The reason might comes from the different thicknesses of the three membranes. As a thick membrane could depress the methanol crossover effect [13], the energy conversion efficiency is thus overwhelmingly large for Nafion 117, which is much thicker than the other two membranes (as described in Section 2.1).

Robustness analysis of operation efficiencies with different membrane types is presented in Fig. 7(b). The evaluated robustness exhibits apparently different variation tendencies as the membrane type changes. For Nafion 115, it grows rapidly up to a relatively large value of 131.7 as the current density varies from 0 to 15.5 mA/cm², and a fluctuation is subsequently experienced in the range of [13.5, 34.9] mA/cm² until a sharp decrease occurs at 36.6 mA/cm². This result indicates that the stability of system efficiency can be maintained at a considerably high level in the moderate operating range of [13.5, 34.9] mA/cm². However, special attention is suggested to be paid at extreme conditions, i.e., the very low (or high) current density, where the stability of system efficiency with Nafion 115 could be diminished to lower the reliability of this power source under disturbed situations [24,25,27]. For Nafion 212, a sudden change in robustness can be observed. It increases dramatically from 110.6 at 15.8 mA/cm² to 372.2 at 17.4 mA/cm² and then rapidly decreases to 213.0 at 19.1 mA/cm². It implies that the stability of system efficiency with Nafion 212 is extremely sensitive to the change of current density. For Nafion 117, although it has presented comparatively high efficiency among the three membrane types (Fig. 7(a)), the evaluated robustness is observed to stay at a relatively low level in the whole range of its operating current density. This result coincides with previous revealings that, a simultaneous maintenance of efficiency and its stability at high levels can be a task full of challenges [11,25,32]. Therefore, the proposed integrated efficiency and robustness evaluations could provide comprehensive information about the energy conversion performances in various DMFCs, which can be very beneficial in the design of optimal operations according to one's specific requirements.

3.4.3. Applications to experimental results

Although the integrated evaluations have been applied to DMFC operations with various MEAs or at different operating conditions, they are all based on the numerical models that are trained by experimental

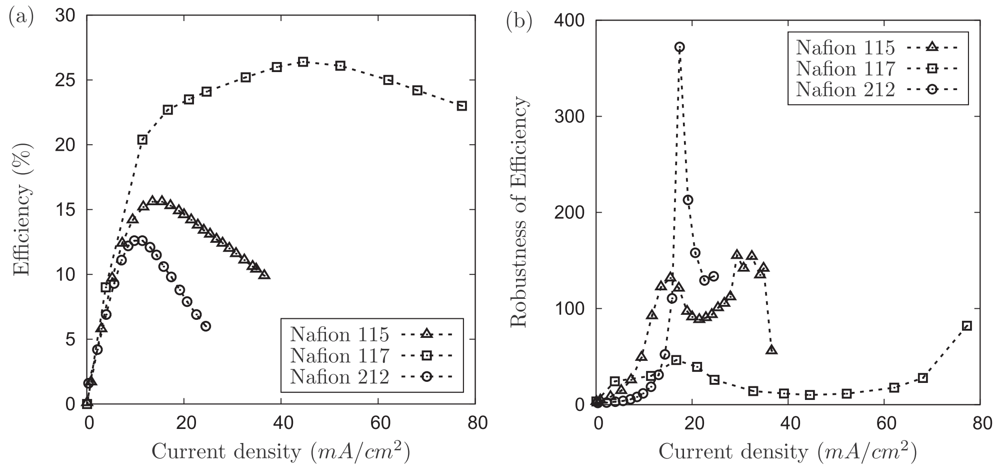

Fig. 7. Integrated efficiency and its extended robustness evaluations in DMFCs with different MEAs.

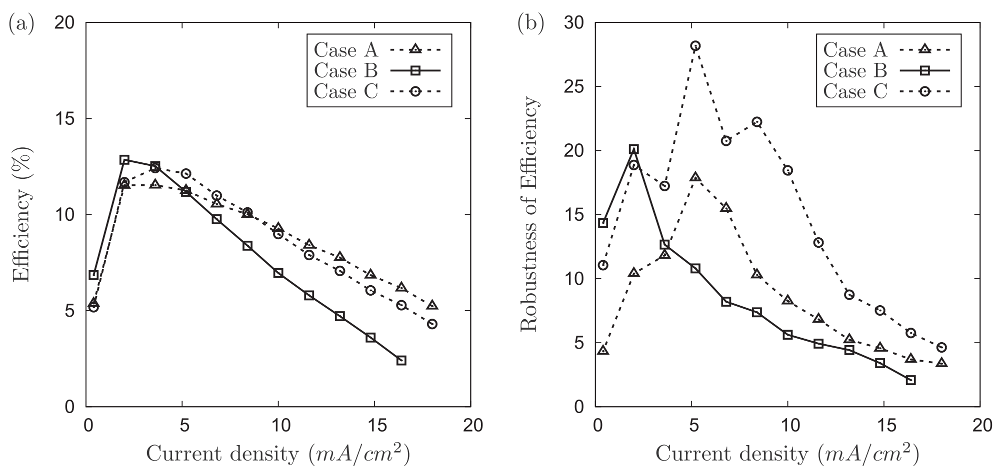

Fig. 8. Integrated efficiency and its extended robustness evaluations in practical DMFC operations. Stable inlet methanol concentration is 2.0, 6.0 and 10.0 ccm in Case A, B and C, respectively, while the corresponding disturbances are available in Table A.4.

data with regular operating parameters. For the purpose of further validating the effectiveness of integrated evaluations, supplementary experiments are performed to consider unusual operating conditions. Specifically, the unusual operating condition is chosen to be extremely large methanol flow rates, as the extreme conditions of temperature or/and input methanol concentration can be detrimental to current MEAs. Large methanol flow rates $F_M = 6$ ccm and 10 ccm are thus considered in the present experiments, compared with the moderate $F_M = 2$ ccm that is frequently encountered in practical uses. The other three operating parameters are kept at $T = 328.2$ K, $C_M = 0.75$ M and $F_A = 600$ ccm. For each stable methanol flow rate, ten times of disturbance (around ± 3.5%) are selected according to random selection in nominal distributions, as summarized in Table A.4. Therefore, overall 30 supplementary experiments are performed based on the single-cell DMFC with Nafion 212 membrane.

Evaluated efficiencies of undisturbed DMFC operations are shown in Fig. 8(a), in which the methanol flow rates for Case A, B and C are 2, 6 and 10 ccm, respectively. At the low current density region ($\leqslant 3.6$ mA/cm^2), the evaluated efficiencies that are close to each others share a very similar increase tendency. It coincides well with previous revealings that the effect of methanol flow rates on energy conversion performance can be ignorable at low current density operations [16,19]. However, the efficiencies are all observed to gradually decrease when the current density is beyond 3.6 mA/cm^2, while the effect of methanol flow rates becomes increasingly significant. Taking Case B for instance, it experiences the highest efficiency among the three cases at low current density, but the situation reverses once the current density is larger than 5.2 mA/cm^2. This result also indicates that the energy conversion efficiency could not monotonically increase with the methanol flow rates. As the manipulation of methanol flow rates is often applied in practice to adjust system power generations [12,16,31], the present result has suggested that special attention needs to be paid on those operational adjustment, as it could generate unpredictable response of energy conversion efficiencies.

Robustness evaluations of disturbed operations with different input methanol flow rates are presented in Fig. 8(b). Unlike the similar tendency observed in evaluated efficiencies, apparent difference can be noticed among the robustness evaluations for the three cases at the low current density region ($\leqslant 3.6$ mA/cm^2). Moreover, the maximum robustness cannot be guaranteed at the same current density, which is 2.0 mA/cm^2 for Case B, and 5.2 mA/cm^2 for Case A and C. At the high current density region ($\geqslant 5.2$ mA/cm^2), all the evaluated robustnesses generally decrease with the increase of current density. It implies that the stability of system efficiency could not be easily maintained if a DMFC is operated at its extreme conditions of high current densities.

Further information can be deduced by an integrated use of efficiency and robustness evaluations. For efficiency-oriented optimizations, the methanol flow rate 2.0 ccm (Case A) can be the best choice among the three cases, as it can provide a relatively stable and efficient output in the whole range of operating current density (Fig. 8(a)). Meanwhile, the robustness of Case A is found to be comparatively high ($\geqslant 10$) in the operating current density range of [2.0, 8.4] mA/cm^2

(Fig. 8(b)). It implies that this operation (Case A) is supposed to be relatively smooth at [2.0, 8.4] mA/cm^2. Therefore, such comprehensive assessments of energy conversion performances could be highly beneficial for optimal selection of appropriate operating condition and working current densities to design stable and efficient DMFC operations.

4. Conclusions

Concentrating on the effects of operational disturbances, a robustness criterion is creatively developed based on the newly modified efficiency criterion, for comprehensive evaluations of the energy conversion process in DMFCs. On the basis of experimental and numerical techniques, careful analyses are performed on classical efficiency criteria. Systematic investigations have also been performed on the integrated use of newly proposed efficiency and robustness evaluations in DMFC systems with different operating conditions and different MEAs. The main findings in the present study can be summarized as follows,

(1) Compared with classical criteria which consider the system efficiency is integrated by several sub-parts, a newly modified efficiency criterion is developed from the global perspective of the whole DMFC systems. It proposes to use Gibbs free energy to substitute the low heating value, which can be beneficial for avoiding misinterpretations of energy conversion process in DMFCs. Comparative study with existing criteria shows that, the newly modified criterion could provide efficient, effective and physically meaningful energy conversion evaluations for undisturbed DMFC operations.
(2) Effect of uncertainty propagations is experimentally revealed to be non-ignorable in disturbed DMFC operations, and it cannot be completely assessed by independently using of efficiency evaluations. A robustness evaluation is then creatively extended from the newly modified efficiency criterion to consider the effects of operational disturbances. Preliminary applications in experimental analysis show that the robustness evaluations provide a guidance to determine the appropriate current densities for stable operations.
(3) Integrated efficiency and robustness evaluations are systematically applied in various conditions, such as different operating parameters and different MEAs. Careful discussions about their feasibility and effectiveness have been well presented. The change of energy conversion performances, which results from either the operational disturbance or the switch of MEAs, can be well differentiated and identified by integrating efficiency and robustness evaluations. Supplementary experiments have also been provided to validate the effectiveness of integrated evaluations in unusual operating conditions. The obtained comprehensive information about energy conversion efficiency and operating stability (robustness) can be highly beneficial for one's optimal design of DMFC operations.

Acknowledgments

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Appendix A. Additional data

See Tables A.3 and A.4.

Table A.3
Disturbed operating parameters in uniform-designed numerical experiments.

Case	*No.*	T (K)	Deviation of T	F_M (ccm)	Deviation of F_M
I	1	305.2	−0.95%	0.47	−6.00%
I	2	313.9	1.86%	0.54	8.00%
I	3	306.0	−0.71%	0.41	−18.0%
I	4	309.1	0.30%	0.52	4.00%
I	5	306.0	−0.69%	0.49	−2.00%
I	6	303.5	−1.50%	0.58	16.00%
I	7	302.6	1.80%	0.49	−2.00%
I	8	307.7	−0.15%	0.52	4.00%
I	9	306.7	−0.49%	0.51	2.00%
I	10	308.0	−0.06%	0.52	4.00%
II	1	315.5	−0.85%	1.54	2.67%
II	2	314.6	−1.13%	1.42	−5.33%
II	3	316.9	−0.41%	1.52	1.33%
II	4	316.2	−0.63%	1.43	−4.67%
II	5	314.2	−1.26%	1.53	2.00%
II	6	323.3	1.60%	1.50	0.00%
II	7	314.0	−1.32%	1.64	9.33%
II	8	317.6	−0.19%	1.55	3.33%
II	9	325.7	2.36%	1.47	−2.00%
II	10	313.4	−1.51%	1.47	−2.00%
III	1	347.2	−0.26%	1.52	1.33%
III	2	349.0	0.24%	1.39	−7.33%
III	3	342.1	−1.74%	1.51	0.67%
III	4	353.6	1.56%	1.45	−3.33%
III	5	347.6	−0.16%	1.51	0.67%
III	6	349.6	4.30%	1.49	−0.67%
III	7	348.5	0.11%	1.53	2.00%
III	8	347.4	−0.22%	1.48	−1.33%

(continued on next page)

Table A.3 (*continued*)

Case	*No.*	*T* (K)	Deviation of *T*	F_M (ccm)	Deviation of F_M
III	9	350.6	0.70%	1.55	3.33%
III	10	349.8	0.47%	1.61	7.33%
IV	1	325.7	−0.73%	2.39	−4.40%
IV	2	326.2	−0.61%	2.43	−2.80%
IV	3	328.1	−0.01%	2.49	−0.40%
IV	4	334.8	2.02%	2.48	−0.80%
IV	5	329.6	0.45%	2.54	1.60%
IV	6	329.1	0.29%	2.50	0.00%
IV	7	330.3	0.65%	2.43	−2.80%
IV	8	321.3	−2.08%	2.49	−0.40%
IV	9	325.9	−0.70%	2.53	1.20%
IV	10	325.6	−0.79%	2.65	6.00%
V	1	306.2	−0.63%	4.39	−2.44%
V	2	309.9	0.56%	4.52	0.44%
V	3	301.4	−2.20%	4.45	−1.11%
V	4	304.5	−1.18%	4.50	0.00%
V	5	309.0	0.27%	4.54	0.89%
V	6	305.3	−0.92%	4.49	−0.22%
V	7	307.3	−2.70%	4.45	−1.11%
V	8	299.1	−2.95%	4.54	0.89%
V	9	311.0	0.90%	4.59	2.00%
V	10	313.0	1.56%	4.52	0.44%

Table A.4
Disturbed operating parameters in experiments.

Case	*No.*	F_M (ccm)	Deviation of F_M	*Case*	*No.*	F_M (ccm)	Deviation of F_M
A	1	1.93	−3.50%	A	2	1.95	−2.50%
A	3	1.97	−1.50%	A	4	1.98	−1.00%
A	5	1.99	−0.50%	A	6	2.00	0.00%
A	7	2.01	0.50%	A	8	2.02	1.00%
A	9	2.03	1.50%	A	10	2.06	3.00%
B	1	5.80	−3.27%	B	2	5.89	−1.90%
B	3	5.92	−1.27%	B	4	5.93	−1.19%
B	5	5.95	−0.90%	B	6	6.00	0.00%
B	7	6.02	0.36%	B	8	6.06	0.99%
B	9	6.09	1.52%	B	10	6.10	1.60%
C	1	9.66	−3.36%	C	2	9.86	−1.39%
C	3	9.89	−1.05%	C	4	9.92	−0.82%
C	5	9.94	−0.56%	C	6	9.95	−0.51%
C	7	9.96	−0.36%	C	8	10.00	0.00%
C	9	10.04	0.44%	C	10	10.14	1.38%

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