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Standardized Procedures Important for Improving Single-Component Ceramic Fuel Cell Technology

The fuel cell is a promising clean energy technology for efficient conversion of fuel to power with no or low emissions (1). It utilizes electrochemical reactions and ion transport to generate electricity through redox-reactions (fuel oxidization, oxygen/air reduction). The main reaction product is water, sometimes also CO_2 depending on the type of fuel used. Fuel cell applications range from small portable devices to medium-scale mobile and stationary uses (2).

Solid oxide or ceramic fuel cells (SOFCs) are a promising fuel cell technology, but they are not yet fully commercial. The limited ionic conductivity of yttrium stabilized zirconia (YSZ) electrolytes used in SOFC requires a high operating temperature (800-1,000°C), which imposes a major challenge on materials, durability, and costs (1). To improve their competitiveness, new pathways have been suggested such the intermediate temperature solid oxide fuel cells (IT-SOFC) (3), which operates below 600 °C. For example, IT-SOFC based on $\text{Ce}_{0.85}\text{Sm}_{0.15}\text{O}_2$ and a eutectic mixture of Na_2CO_3 , Li_2CO_3 , K_2CO_3 has reached $1.1\text{W}/\text{cm}^2$ at 550°C (4). Another interesting development is the so-called single component fuel cell, which employs a mixture of ionic conductor and semiconductor materials, e.g. a perovskite $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) and Sm-Ca-co-doped ceria (SCDC) nanocomposite heterostructure (5), semiconductor-ionic $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}-\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ composite (6), or Sm-doped ceria (7) and NiZn-oxide nanocomposite material system. Instead of a traditional 3-layer fuel cell structure, the single-component approach integrates the cathode, electrolyte, and anode into one homogenous structure and one material called 3-in-1 (8). The SCDC-LSCF n-p heterojunction separates holes and electrons preventing short-circuiting or electrochemical leakage, whereas SCDC is also ion conducting (O^{2-} , H^+) (see Fig.1) (6). Other materials of similar interest include e.g. YSZ-SrTiO₃ (9,10) and SDC-SrTiO₃ (7). Several research groups have demonstrated that such devices work satisfactorily. Similarly it has been reported that LiCoAlO_2 (11) and SmNiO_3 (12) oxides experience a transition from a semiconductor to a H^+ ionic conductor under fuel cell conditions. Performance results reported are around $500\text{-}600\text{W}/\text{cm}^2$ at 500°C , the best exceeding $1\text{W}/\text{cm}^2$ (6). The traditional solid oxide fuel cell technology closest to this design reaches $300\text{-}400\text{W}/\text{cm}^2$ at 700°C . The lower operational temperature, high power density, and only one material layer make the single-component fuel cells an interesting alternative for low-cost mass-production.

Based on reported characteristics and promising single cell results, the single-component fuel cell could possess potential for a technological breakthrough, but it is still hampered by some fundamental questions such as repeatability of experiments reported, lacking broader theoretical explanation of experiments albeit tentative efforts in this direction, inconsistencies in experimental set-ups, differences in device configurations, and varying reporting practices of results, many of which could, however, be overcome through more systematic research and more standardized research procedures. The theoretical background of the operational principle is also still under discussion (13,14).

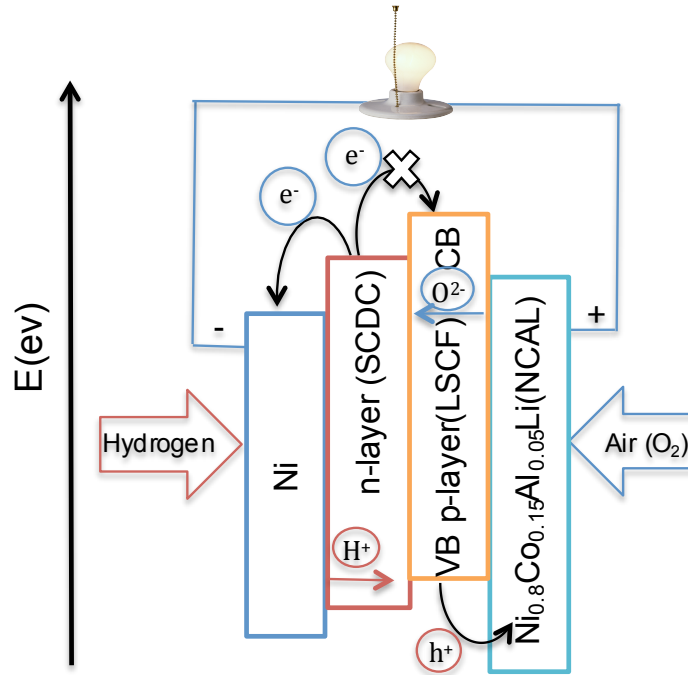
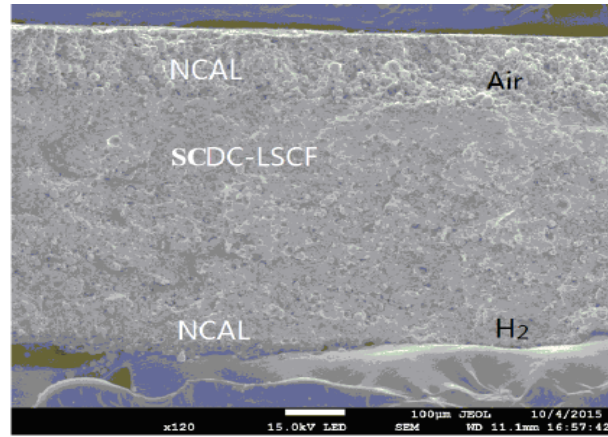


Figure 1. Principle of a single-component fuel cell. The SCDC(n)-LSFC(p) heterojunction layer prevents electron flow through the device, SCDC(ion) also exhibits ionic conductivity; Ni and NCAL(p) are current collectors. Upper figure is from Ref.(6) with permission by Elsevier 2017.

We found several potential random and systematic error sources in reported research, which could add major uncertainties to performance results and complicate comparison of different experiments or singling out the impact of different factors on the fuel cell performance. For example, one error source is related to cell geometry (diameter, thickness), which affects the area-dependent parameters typically used in reporting the performance, e.g. power or current density (Wcm^{-2} , Acm^{-2}), area specific resistance (Ωcm^2), and thickness-dependent cell resistance ($\Omega\text{cm}^{-1}\times\text{cm}$). Small button cells are used in laboratory measurements, meaning that even a small inaccuracy in measuring the diameter of the active area could lead to a notable error, for example with $\text{Ø}=13\text{mm}$ and $\Delta\text{Ø}=1.3\text{ mm}$ a 20% uncertainty could result. Ionic conductivity is reported per unit thickness ($\Omega^{-1}\text{cm}^{-1}$) from measured cell or layer resistivity and thickness, meaning that any uncertainty in the thickness value would directly find itself in the ionic conductivity value. For example, a typical thickness of reported cells is 1-3mm and a measurement inaccuracy of 0.2-0.3mm results in a 10-40% error margin. Another source of uncertainty relates to accurately determining

the cell temperature when measuring the performance of the cell in a chamber (15). As the single-component fuel cell is based on a solid conductor, its ionic conductivity strongly depends on the temperature ($\ln\sigma \sim -T^{-1}$), meaning that at a typical operational temperature of 500-550°C, a 20°C measurement inaccuracy could lead to a uncertainty of -20...+30% in σ . If the material had a carbonate component, this could be even more critical due to their phase change in this temperature range, which could significantly affect ionic conductivity.

We demonstrate the effect of above uncertainties on the performance of a single-component fuel cell in Fig. 2, where we modeled the fuel cell performance against uncertainties based on measured performance in stoichiometric conditions at 550 °C. Accounting for the uncertainties in cell area (+/-10%) and temperature (+/-20°C) could result in -15%...35% uncertainty in the power density, and in an even larger span in the cell voltage.

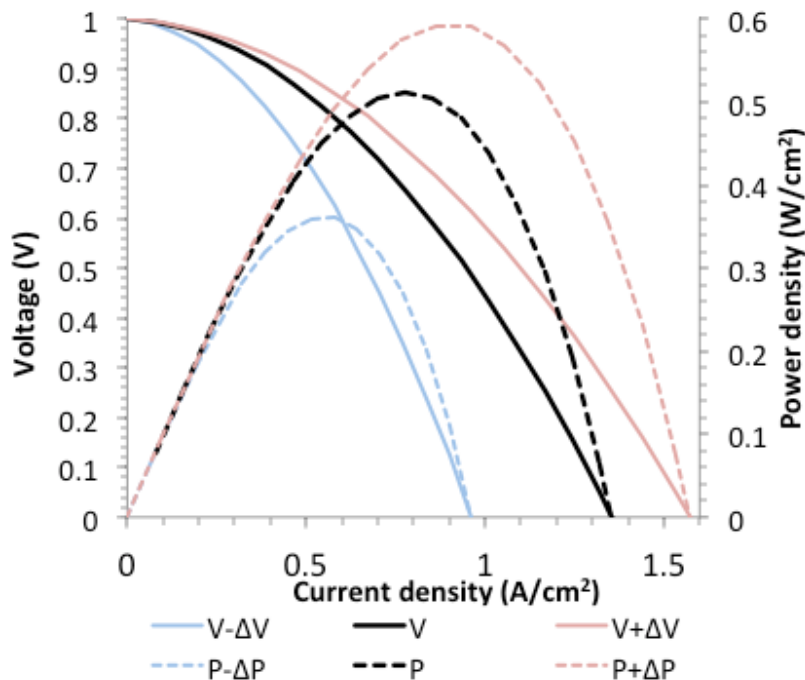


Figure 2. Effect of measurement inaccuracies (temperature, diameter of active cell) on the performance of a single-component fuel cell based on a modeling exercise.

When reporting the Open Circuit Voltage (OCV), Current-Voltage (I-V) or Power-Voltage (P-V) curves of the fuel cell, the measurement conditions should be carefully and clearly reported, and stoichiometric or standard conditions (partial pressures) should preferably be employed to enable easy comparison. Also, in the measurement situation itself, it is important to measure in static conditions avoiding transient behavior, which could easily distort results. It would also be important to ensure that only fuel cell reactions are measured, as other catalytic reactions may also be involved in the device.

Previous studies indicate that ionic conductivities of similar composite fuel cell materials measured under similar conditions vary quite much, which could be partly explained by the sample preparation affecting the properties of the electrolyte and by the used measurement approach indicating that results from different ionic

conductivity measurement techniques may not always be comparable (16). The preparation method of the fuel cell material and the sample pellet affect largely the ionic conductivity and performance, e.g. the homogeneity of the material, the size of the particles, the relative density of the pellet, and grain boundary framework. Possible impurities can also segregate to the boundaries adding extra resistance. Surface defects may influence both ionic and electronic conductivity. Fuel cell measurements are commonly done with a 2-point configuration due to easy implementation, but this would require several measurements for accuracy, whereas with the 4-point method polarizations due to the electrodes can be neglected, though effects from the potential distribution need still to be considered. Again, to enable comparison between different studies of single-component fuel cells and better understanding of reasons for differences, both the cell preparation and measurement approaches should be documented in more detail than presently.

Improving the reporting quality of results and moving toward standardized experimental procedures would also be important to enable better linkage between experimental and theoretical work. The principle of the single-component is not unambiguous, though presently assumed to be based on Schottky-barrier structure (17) and nano-redox processes (ORR oxygen reduction and HOR hydrogen oxidation reactions) (18) on nanocomposite particle surfaces, but a full theoretical clarity of the principle is still lacking. Therefore using more sophisticated theory tools such as computational quantum mechanical modelling (e.g. first-principle density functional theory (DFT) calculations and *ab initio* Car–Parrinello molecular dynamics (CPMD) simulations) could shed light to better understanding functional principles and properties, and interface transport phenomena on an atomic and molecular level. 3D microscopy and tomography would be helpful to link structures and performance relations, but this would also call for well-mastered experiments (19). Advanced material configurations in atomic scale could also be of interest to improve single-component fuel cells employing advanced thin-film deposition techniques, tailored nanostructures, more effective catalysts, carbon nanomaterials, etc. For example Atomic Layer Deposition (ALD) enables constructing topological interfaces and catalysts, which could enhance fuel cell performance. Thus, to be able to assess the effects from advanced materials on the performance, the uncertainty of the measurements needs to be suppressed. This would also call for better consideration of the measurement statistics, as too often results of a single sample only, and even a single or just a few measurements are reported.

Moving single-component fuel cell technology towards real-world applications would also require more consideration on stability, scale-up, and engineering (composition, interface, molecule engineering, etc.) The performance measurements of laboratory cells seldom address stability over time. At best the stability of the cell and material is reported for just a few hundred hours, which is too short for practical applications. Degradation mechanisms should be considered more by the research even in lab-scale, because this is highly relevant to scaling-up of the technology. Scaling-up of button cells from $\varnothing < 20\text{mm}$ to cell sizes relevant to small stack designs e.g. to $6\text{cm} \times 6\text{cm}$ may introduce new features such as inhomogeneity and spatial effects absent in small scale, which need to be addressed when moving to practical applications.

In addition to using more advanced materials and scientific methods and tools, equally important would be to work out a more systematic way with standardized procedures and make better use of resources to accelerate progress of this new fuel cell technology. We think it would be important to pay attention in particular to the following three main issues:

1. Documentation (sample geometry, materials, material synthesis and cell fabrication methods and conditions, performance conditions)
2. Management (planning, execution, analysis of experiments)
3. Error sources (geometry, temperature, impurities, transients)

For the international community working in this field it would be useful pursuing towards more standard practices and procedures in the three areas above. For this purpose, we propose a framework in Table 1, which incorporates major improvements to current practices in the field and could contribute to reducing the uncertainties of reported results, increase repeatability of experiments, and their reliability.

Table 1. Framework of procedures for single-component fuel cell experiments.

	Sample fuel cells	Experimental setup	Performance measurements
Issues of concern	Sample geometry and dimensions	Cell temperature	Error estimates
	Sample composition and impurities	Wiring arrangements	Non-transient measurement region
	Sample preparation	Gas mixture	Cell stability
	Standardized samples	Calibration	Number of cells in measurement and measurements per sample
Recommendations	0.1mm resolution of measuring dimensions, or <5% of measures	Cell surface temperature measurement	5 samples of each type, 3 repeated measurements of each sample at each data point (e.g. temperature, current)
	Masking of active area of samples	4-point electrochemical measurements	2-3 hours stabilization before starting recording values
	Reporting all ingredients and grades	Stoichiometric conditions	Performance values with error estimates
	Step-by-step reporting of sample manufacturing	Calibration of fuel cell test station with known reference samples	
	Making available reference samples for open access	Proper gas sealing of the measurement chambers	
	Measurement conditions mimicking real-world conditions		

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