

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

- **Corresponding Author**

- **Peter D. Lund** - *School of Science, Aalto University, P.O. Box 15100, 00076 Aalto, Espoo, Finland*; <http://orcid.org/0000-0002-4819-3847>; Email: peter.lund@aalto.fi

- **Authors**

- **Bin Zhu** - *Department of Energy Technology, KTH Royal Institute of Technology, Stockholm 10044, Sweden; Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Faculty of Physics and Electronic Science, Hubei University, Wuhan 430062, China*; <http://orcid.org/0000-0003-1479-0464>
- **Yongdan Li** - *School of Chemical Engineering, Tinjian University, Tinjian 300072, China; School of Chemical Engineering, Aalto University, P.O. Box 16100, FI-00076 Aalto, Espoo, Finland*
- **Sining Yun** - *School of Materials & Mineral Resources, Functional Materials Laboratory (FML), Xi'an University of Architecture and Technology, Xi'an, Shaanxi 710055, China*
- **Albert G. Nasibulin** - *Laboratory of NanoMaterials, Skolkovo Institute of Science and Technology, Moscow 143026, Russia; School of Science, Aalto University, P.O. Box 15100, 00076 Aalto, Espoo, Finland*
- **Rizwan Raza** - *COMSATS Institute of Information Technology, Lahore 54000, Pakistan*
- **Markku Leskelä** - *Department of Chemistry, University of Helsinki, P.O. Box 55, FI-00014 University of Helsinki, Helsinki, Finland*
- **Meng Ni** - *Department of Building and Real Estate, Hong Kong Polytechnic University, Kowloon, Hong Kong*
- **Yan Wu** - *China University of Geosciences, Wuhan 430074, China*; <http://orcid.org/0000-0002-1252-5600>
- **Gang Chen** - *School of Metallurgy, Northeastern University, Shenyang 110819, China*
- **Liangdong Fan** - *College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518060, Guangdong, China*
- **Jung-Sik Kim** - *Department of Aeronautical & Automotive Engineering, Loughborough University, Loughborough LE113TU, United Kingdom*
- **Suddhasatwa Basu** - *Indian Institute of Technology, New Delhi 110016, India*
- **Tanja Kallio** - *School of Chemical Engineering, Aalto University, P.O. Box 16100, FI-00076 Aalto, Espoo, Finland*; <http://orcid.org/0000-0001-6671-8582>
- **Ibrahim Pamuk** - *Vestel Defence Industry, Golbasi, Ankara 06830, Turkey*

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 CO₂ 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 SOFCs requires a high operating temperature (800–1000 °C), which imposes a major challenge on materials, durability, and costs. (1) To improve their competitiveness, new alternatives have been suggested, such as the intermediate temperature solid oxide fuel cells (IT-SOFCs), (3) which operates below 600 °C. For example, IT-SOFCs based on Ce_{0.85}Sm_{0.15}O₂ and a eutectic mixture of Na₂CO₃, Li₂CO₃, K₂CO₃ have reached 1.1 W/cm² 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 La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF) and Sm–Ca-co-doped ceria (SCDC) nanocomposite heterostructure, (5) semiconductor–ionic Sr₂Fe_{1.5}Mo_{0.5}O_{6-δ}–Ce_{0.8}Sm_{0.2}O_{2-δ} composite, (6) or Sm-doped ceria (7) and NiZn-oxide nanocomposite material systems. Instead of a traditional 3-layer fuel cell structure, the single-component approach integrates the cathode, electrolyte, and anode into one homogeneous 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 (O²⁻, H⁺) (see Figures 1 and 2). (6) Other materials of similar interest include, for example, YSZ-SrTiO₃ (9, 10) and SDC-SrTiO₃. (7) Several research groups have demonstrated that such devices work satisfactorily. Similarly, it has been reported that LiCoAlO₂ (11) and SmNiO₃ (12) oxides experience a transition from a semiconductor to a H⁺ ionic conductor under fuel cell conditions.

Performance results reported are around 500–600 W/cm² at 500 °C, with the best exceeding 1 W/cm². [\(6\)](#) The traditional SOFC technology closest to this design reaches 300–400 W/cm² at 700 °C. [\(13\)](#) 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.

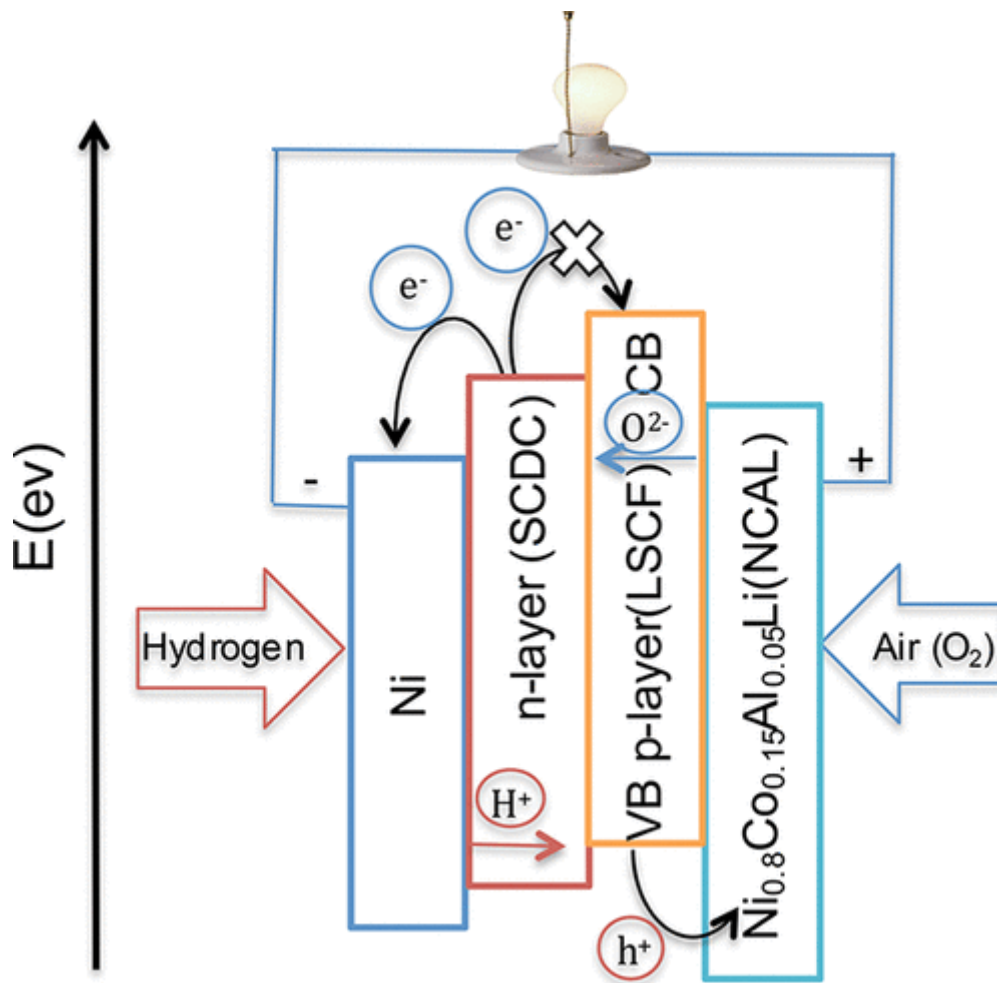


Figure 1. Principle of a single-component fuel cell. [\(6\)](#) The SCDC(n)–LSFC(p) heterojunction layer prevents electron flow through the device, and SCDC(ion) also exhibits ionic conductivity; Ni/NCAL(p) is current collector.

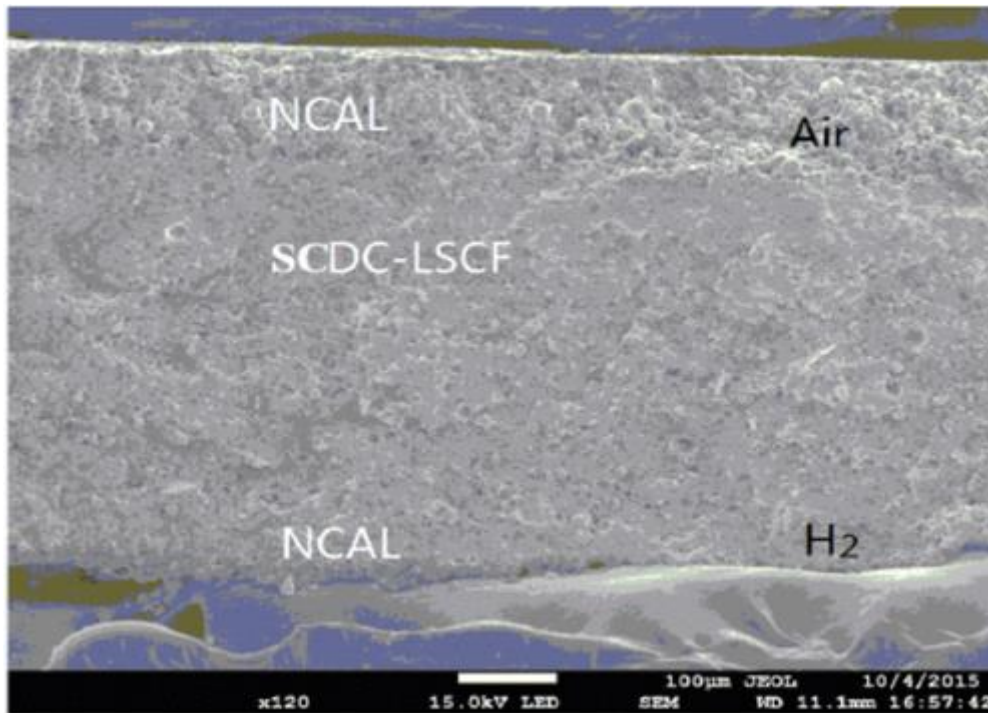


Figure 2. SEM micrograph of a single-component fuel cell. Reproduced with permission from ref [6](#). Copyright 2017 Elsevier.

On the basis of 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 (although there are tentative efforts in this direction), inconsistencies in experimental setups, 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. ([14, 15](#))

We found several potential sources of random and systematic errors in reported research, which could add major uncertainties to performance results and complicate comparison of different experiments, singling out the impact of different factors on the fuel cell performance, and determining the state-of-the-art stand of the technology. 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 (W cm^{-2} , A cm^{-2}), area-specific resistance ($\Omega \text{ cm}^2$), and thickness-dependent cell resistance ($\Omega \text{ cm}^{-1} \times \text{cm}$). Little button cells are used in laboratory measurements, meaning that even a small inaccuracy in determining the diameter of the active area could lead to a notable error, for example, with $\varnothing = 13 \text{ mm}$ and $\Delta\varnothing = 1 \text{ mm}$ could result in a 17% uncertainty in the area. Ionic conductivity is reported per unit thickness ($\Omega^{-1} \text{ cm}^{-1}$) and determined 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 1–3 mm, and a measurement inaccuracy of 0.2–0.3 mm would result in a 10–30% error margin in the ionic conductivity.

Another source of uncertainty relates to accurately determining the cell temperature when measuring the performance of the cell in a chamber. [\(16\)](#) As the single-component fuel cell is based on a solid conductor, its ionic conductivity strongly depends on the temperature ($\ln \sigma \propto T^{-1}$), meaning that at a typical operational temperature of 500–550 °C, a 20 °C measurement inaccuracy could lead to an uncertainty of $\pm 10\%$ in σ . If the operating temperature were decreased to 400 °C and had the material a carbonate component, this could be even more critical because of the phase change of carbonates in this temperature range, which could significantly affect the ionic conductivity. [\(4\)](#)

We demonstrate the effect of above uncertainties on the performance of a single-component fuel cell in [Figure 3](#), where we modeled the fuel cell performance against uncertainties based on measured performance in stoichiometric conditions at 550 °C. Accounting for the uncertainties in the cell area ($\pm 10\%$), thickness ($\pm 10\%$), and temperature ($\pm 20 \text{ °C}$) could result in an uncertainty range from -19% to $+21\%$ in the maximum power density, and in an even larger span at high current density.

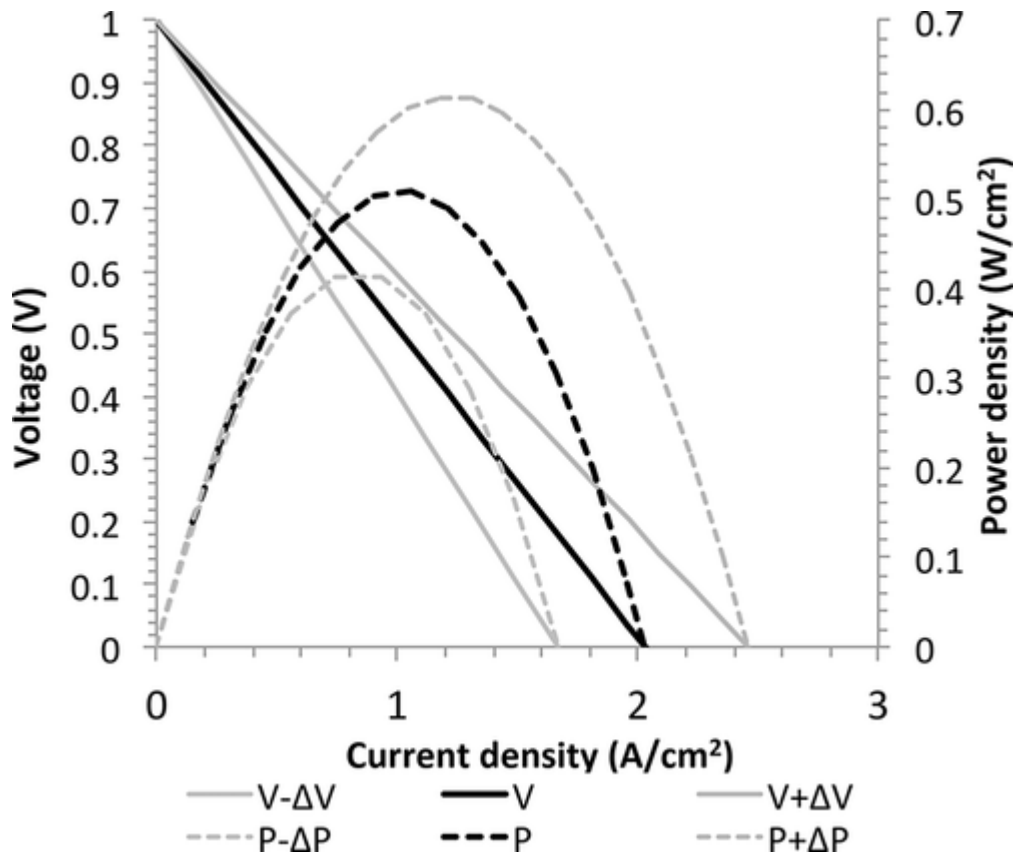


Figure 3. Effect of measurement inaccuracies (temperature, diameter of active cell) on the performance of a single-component fuel cell based on a modeling exercise.

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. In addition, in the measurement situation itself, it is important to measure in static conditions avoiding transient behavior, which could easily distort results. It would 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 considerably, which could partly be 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. [\(17\)](#) The preparation method of the fuel cell material and the sample pellet largely affects 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 because of 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 as well as the contact resistances. 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 is presently provided.

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 [\(18\)](#) and nanoredox processes [oxygen reduction (ORR) and hydrogen oxidation (HOR) reactions] [\(19\)](#) 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 modeling [e.g., first-principle density functional theory (DFT) calculations and ab initio Car–Parrinello molecular dynamics (CPMD) simulations] could shed light to better understanding the functional principles and properties and interface transport phenomena on an atomic and molecular level. Comprehensive electrochemical analysis of Faradaic losses could be useful to determine possible unwanted side reactions, e.g., those linked to electron leakage. Three-dimensional microscopy and tomography would be helpful to link structures and performance relations, but

this would call for well-mastered experiments. [\(20\)](#) Advanced material configurations on the 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, or even a single or just a few measurements, are reported.

Moving single-component fuel cell technology toward real-world applications would also require more consideration on stability, scale-up, and engineering (composition, interface engineering, etc.). 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, but the measurement period may even remain unreported. 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 ($\varnothing < 20$ mm) to cell sizes relevant to small stack designs, e.g., to $6\text{ cm} \times 6\text{ cm}$ planar cells, may introduce new features such as inhomogeneity and spatial effects absent in the small scale and which need to be addressed when moving to practical applications. Also, test procedures for cells and stacks would need to be elaborated.

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 making 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 to strive toward more standard practices and procedures in these three areas. For this purpose, we propose a framework in [Table 1](#), which incorporates major improvements to current practices and could result in reducing the uncertainties of reported results and 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	nontransient measurement region
	sample preparation	gas mixture	cell stability
	standardized samples	calibration	number of cells in a measurement and measurements per sample
recommendations	<5% inaccuracy in measuring cell dimensions	cell temperature measurement	5 samples of each type, 3 parallel measurements of each sample at each data point (e.g., temperature, current)
	masking of active area of samples	4-point electrochemical measurements	2–3 h stabilization before starting recording values

sample fuel cells		experimental setup	performance measurements
reporting ingredients and grades	all and	stoichiometric conditions	performance values with error estimates
step-by-step reporting of material synthesis and sample manufacturing		calibration of fuel cell test station with known reference samples	
providing access to reference samples	open to	proper gas sealing of the measurement chambers	
		measurement conditions mimicking real-world conditions	

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References

1.

Steele, B. C.; Heinzl, A. Materials for fuel-cell technologies *Nature* **2001**, 414, 345– 52 DOI: 10.1038/35104620

2.

Wilberforce, T.; Alaswad, A.; Palumbo, A.; Dassisti, M.; Olabi, A. G. Advances in stationary and portable fuel cell applications Int. J. Hydrogen Energy **2016**, 41, 16509– 22 DOI: 10.1016/j.ijhydene.2016.02.057

3.

Shin, J. F.; Xu, W.; Zanella, M.; Dawson, K.; Savvin, S. N.; Claridge, J. B.; Rosseinsky, M. J. Self-assembled dynamic perovskite composite cathodes for intermediate temperature solid oxide fuel cells Nat. Energy **2017**, 2, 16214 DOI: 10.1038/nenergy.2016.214

4.

Asghar, M. I.; Heikkilä, M.; Lund, P. D. Advanced low-temperature ceramic nanocomposite fuel cells using ultra high ionic conductivity electrolytes synthesized through freeze-dried method and solid-route Mater. Today Ene. **2017**, 5, 338– 46 DOI: 10.1016/j.mtener.2017.07.017

5.

Wang, B.; Wang, Y.; Fan, L.; Cai, Y.; Xia, C.; Liu, Y.; Raza, R.; van Aken, P.; Wang, H.; Zhu, B. Preparation and characterization of Sm and Ca co-doped ceria $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-d}$ semiconductor-ionic composites for electrolyte-layer-free fuel cells J. Mater. Chem. A **2016**, 4, 15426– 15436 DOI: 10.1039/C6TA05763B

6.

Zhu, B.; Wang, B.; Wang, Y.; Raza, R.; Tan, W.; Kim, J.-S.; van Aken, P. A.; Lund, P. Charge separation and transport in $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-d}$ and ion-doping ceria heterostructure material for new generation fuel cell Nano Energy **2017**, 37, 195– 202 DOI: 10.1016/j.nanoen.2017.05.003

7.

Yang, S. M.; Lee, S.; Jian, J.; Zhang, W.; Lu, P.; Jia, Q.; Wang, H.; Noh, T. W.; Kalinin, S. V.; MacManus-Driscoll, J. L. Strongly enhanced oxygen ion transport through samarium-doped CeO₂ nanopillars in nanocomposite films Nat. Commun. **2015**, 6, 8588 DOI: 10.1038/ncomms9588

8.

Nature nanotechnology research highlights. Fuel cells: Three in one. Nat. Nanotechnol. **2011**, 6, 330. DOI: DOI: 10.1038/nnano.2011.93 .

9.

Garcia-Barriocanal, J.; Rivera-Calzada, A.; Varela, M.; Sefrioui, Z.; Iborra, E.; Leon, C.; Pennycook, S. J.; Santamaria, J. Colossal ionic conductivity at interfaces of epitaxial ZrO₂:Y₂O₃/SrTiO₃ heterostructures Science **2008**, 321, 676– 680 DOI: 10.1126/science.1156393

10.

Kilner, J. A. Ionic conductors: Feel the strain Nat. Mater. **2008**, 7, 838– 839 DOI: 10.1038/nmat2314

11.

Lan, R.; Tao, S. Novel proton conductors in the layered oxide material Li_xAl_{0.5}Co_{0.5}O₂ Adv. Energy Mater. **2014**, 4, 1301683 DOI: 10.1002/aenm.201301683

12.

Zhou, Y.; Guan, X.; Zhou, H.; Ramadoss, K.; Adam, S.; Liu, H.; Lee, S.; Shi, J.; Tsuchiya, M.; Fong, D. D.; Ramanathan, S. Strongly correlated perovskite fuel cells *Nature* **2016**, 534, 231– 34 DOI: 10.1038/nature17653

13.

Krishnan, V. V. Recent developments in metal-supported solid oxide fuel cells *WIREs Energy Environ* **2017**, 6, e246 DOI: 10.1002/wene.246

14.

Hwang, H. Y.; Iwasa, Y.; Kawasaki, M.; Keimer, B.; Nagaosa, N.; Tokura, Y. Emergent phenomena at oxide interfaces *Nat. Mater.* **2012**, 11, 103– 113 DOI: 10.1038/nmat3223

15.

Lorenz, M.; Ramachandra Rao, M. S.; Venkatesan, T.; Fortunato, E.; Barquinha, P.; Branquinho, R.; Salgueiro, D.; Martins, R.; Carlos, E.; Liu, A. The 2016 oxide electronic materials and oxide interfaces roadmap *J. Phys. D: Appl. Phys.* **2016**, 49, 433001 DOI: 10.1088/0022-3727/49/43/433001

16.

Guk, E.; Ranaweera, M.; Venkatesan, V.; Kim, J.-S. Performance and durability of thin film thermocouple array on a porous electrode *Sensors* **2016**, 16, 1329 DOI: 10.3390/s16091329

17.

Patakangas, J.; Ma, Y.; Jing, Y.; Lund, P. Review and analysis of characterization methods and ionic conductivities for low-temperature fuel cells (LT-SOFC) *J. Power Sources* **2014**, 263, 315– 31 DOI: 10.1016/j.jpowsour.2014.04.008

18.

Zhu, B.; Lund, P. D.; Raza, R.; Ma, Y.; Fan, L.; Afzal, M.; Patakangas, J.; He, Y.; Zhao, Y.; Tan, W. Schottky junction effect on high performance fuel cells based on nanocomposite materials *Adv. Energy Mater.* **2015**, 5, 1401895 DOI: 10.1002/aenm.201401895

19.

Zhu, B.; Lund, P.; Raza, R.; Patakangas, J.; Huang, Q.-A.; Fan, L.; Singh, M. A new energy conversion technology based on nano-redox and nano-device processes *Nano Energy* **2013**, 2, 1179– 85 DOI: 10.1016/j.nanoen.2013.05.001

20.

Xia, X.; Yates, J. L. R.; Jones, G.; Sarwar, M.; Harkness, I.; Thompsett, D. Theoretical exploration of novel catalyst support materials for fuel cell applications *J. Mater. Chem. A* **2016**, 4, 15181– 8 DOI: 10.1039/C6TA05399H