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Single Chamber Fuel Cells: Flow Geometry, Rate and Composition Considerations

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ABSTRACT

Four different single chamber fuel cell designs were compared using propane-air gas mixtures. Gas flow around the electrodes has a significant influence on the open circuit voltage and the power density of the cell. The strong influence of flow geometry is likely due to its effect on gas composition, particularly on the oxygen chemical potential at the two electrodes as a result of gas mixing. The chamber design which exposes the cathode first to the inlet gas was found to yield the best performance at lower flow rates, while the open tube design with the electrodes equally exposed to the inlet gas worked best at higher flow rates.

INTRODUCTION

Single chamber fuel cells (SCFCs) have no seal separating the anode and cathode, and consequently both electrodes are simultaneously exposed to the fuel/air mixture. Although SCFCs were proposed more than four decades ago,^{1,2} only recently have these devices surpassed the level of laboratory curiosity by achieving electrode power densities comparable to those of the much more studied dual chamber, sealed cells.^{3,4} While the SCFC research is still at an early stage, new applications are emerging, such as simple low-power sources⁵ and hydrocarbon sensors.⁶

The principle of operation for a single chamber fuel cell is based on the different electrocatalytic properties of fuel cell electrodes toward anodic oxidation of fuel and cathodic reduction of oxygen, respectively, thus resulting in an EMF even in a uniform atmosphere containing

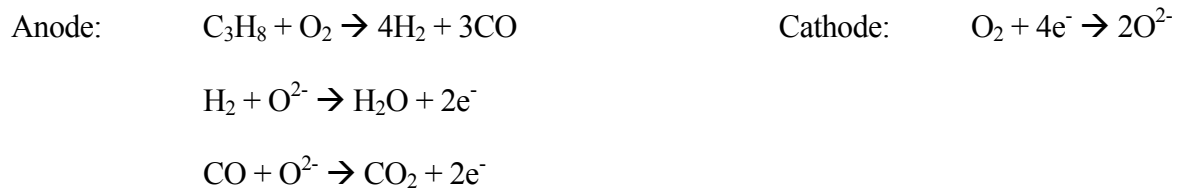
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a fuel and an oxidant. This type of fuel cell simplifies considerably the high temperature sealing requirements which affect conventional solid oxide fuel cells (SOFCs); this can be a significant advantage in that sealing is one of the key technical hurdles in SOFC development. Furthermore, the solid electrolyte does not have to be pore-free, as leaks are of no concern, allowing for thermally and mechanically more shock resistant designs.

As shown by Riess et al.,⁷ similar to conventional fuel cells, SCFCs using oxygen O²⁻ conductor solid electrolytes are driven by the chemical potential difference

$$\Delta\mu_{O_2} = \mu_{O_2}(\text{Cathode}) - \mu_{O_2}(\text{Anode})$$

determined by the gas composition at the two electrodes, resulting in a concentration gradient of O²⁻ ions across the solid electrolyte. In the case of SCFCs, the gas composition at the two electrodes is different due to the various reactions catalyzed by each of the electrodes. For example, it was shown that the concentration of oxygen is zero in the vicinity of the anode in a SCFC working on methane-air gas mixture,⁸ due to partial oxidation reactions of methane at the anode. In the case of a propane-air mixture, used in our studies, the following reactions should proceed at the electrodes resulting in a voltage across the cell:



SCFCs are usually run on rich fuel-air mixtures, which allows total consumption of O₂ at the anode and thus, a maximum gradient across the cell (provided that the cathode is inert to oxidation of fuel reactions). It seems thus reasonable to assume that, although initially uniform, mixing of gases after they pass over the electrodes with inlet gases decreases the oxygen concentration gradient across the electrolyte and the performance of the cell. Indeed, Bay and coworkers⁹ have shown that a

single chamber fuel cell design which prevents mixing of gases entering the cell chamber with those having passed over the electrodes improves the performance of the cell by about five times (although the increase in performance was attributed to a decrease in electrode poisoning).

Experiments done in our laboratory have shown that the performance of a single chamber fuel cell is dependent on the physical-geometrical parameters of the experimental setup, such as the position of the cell with respect to the fuel-air mix flow, the total flow rate and the fuel/air ratio, in addition to the fuel cell microstructure.

EXPERIMENTAL

Thick electrolyte cells were processed together to minimize differences introduced during cell fabrication. Single chamber fuel cells were constructed in a manner similar to those reported by Hibino et al.³ $\text{Sm}_{0.22}\text{Ce}_{0.78}\text{O}_{3-x}$ (SDC) powder from Rhodia Inc., with a particle size of 0.3 μm and a surface area of 33.8 m^2/g , was ultrasonicated in isopropyl alcohol (IPA) with 2 %wt of a polyvinylbutyral (PVB) binder. The solvent was evaporated while stirring, and the resulting solids were ground with mortar and pestle, and passed through a 150 μm screen sieve. The resulting powder was then uniaxially pressed at 10 kpsi in a 1/2" stainless steel die. The pressed disks were sintered at 1450°C for 4 hours, and polished using 1 μm alumina powder to a thickness of 0.8 mm.

NiO (99%, J.T. Baker) and SDC powders in a ratio of 60:40 were attritor milled for 1 hr, at 550 rpm, with 1 wt% Menhaden fish oil in IPA, using zirconia milling balls. The mixture was dried while stirring, ground with mortar and pestle, and also passed through a 150 μm screen sieve. 10 ml of a suspension of 2.5%wt of NiO-SDC powder in IPA was spray painted on one side of each of the SDC disks, masked with tape to define a square area of 0.25 cm^2 , constituting the anode. The painted disks were fired at 1200°C for 2 hours, producing a porous anode with a thickness of about 15 μm . The NiO was reduced to Ni under a 50 cm^3/min H_2 flow, at 600°C, for 30 min, before fuel cell

testing.

The cathode was made of $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-x}$ (SSC) powder, obtained by the glycine-nitrate combustion method¹⁰ from the corresponding metal nitrates (Sigma-Aldrich). The combusted SSC powder was calcined at 1000°C for 2h, and attritor milled for 1 hr at 550 rpm, with SDC (70:30 ratio by weight) and fish oil (1 wt%), using zirconia milling balls in IPA. The mixture was dried while stirring, ground with mortar and pestle, and passed through a 150 μm screen sieve. The thin film cathode was deposited by the same method as the anode, and sintered at 950°C for 2 hours, producing a porous anode with a thickness of about 15 μm .

A Pt mesh attached with Pt paste (Heraeus) was used as the anode current collector, and Au mesh and paste were used similarly for the cathode. The mesh current collectors were spot welded to Pt wires in the fuel cell test tube.

Fuel cells fabricated as described above were tested in the single chamber configurations shown in Figure 1, in propane-air mixtures of different ratios and flows, at 600°C. Gas flows were set to desired values using MKS mass flow controllers (Type 247), controlled by a LabView application on PC, which also controlled the potentiostat (EG&G 371) used for fuel cell performance tests. Temperature was controlled and monitored during the test by a thermocouple placed inside the test rig tube, a few mm away and downstream from the cell.

RESULTS AND DISCUSSION

Single chamber fuel cell tests were conducted in a similar fashion in all four configurations shown in Figure 1A-D, to be referred as closed tube parallel (A), open tube parallel (B), open tube cathode first (C), and open tube anode first (D). The total flow rate was increased to a maximum value for each propane/air ratio, starting with the least rich ratio, in steps of 2.5 cm^3/min propane, from 0 to 50 cm^3/min (the range allowed by the flow controller), and the open circuit voltage (OCV)

of the cell was recorded after equilibration for each flow rate and fuel ratio. After all flow rates and gas compositions were tested, the cell was current conditioned at 50 mA/cm^2 for 1 hour, and then the performance of the cells in each of the four configurations was evaluated.

Although previous SCFC tests in our laboratory suffered from carbon deposition in similar conditions, it was found that this can be avoided by reducing the anode thickness to about $15 \text{ }\mu\text{m}$ (or less). Higher $\text{O}_2:\text{C}_3\text{H}_8$ ratios also reduce the chance of carbon deposition, and water produced by total oxidation reactions or by electrode reaction keeps the electrode free of carbon deposits. Examination of the cells tested during these studies using optical and electron microscopes showed no carbon deposits.

Flow rate effect. As can be seen in Figure 2 A-D, the OCV dependence on the flow rate has a different shape for each of the four test configurations. It can be noticed, however, that it is possible to get similar OCV values in all configurations, provided that the appropriate flow rate is selected. For example, in the closed tube test (Figure 2A), due to mixing at the end of the tube, a high flow rate is necessary to provide a gas mixture with oxygen content close to that of the inlet composition, which is the highest possible in all cases (any reaction, in the gas phase or at the electrodes, decreases the oxygen partial pressure). In the case of the open tube parallel test, the OCV increases monotonically with flow rate, with a change in slope at about $100 \text{ cm}^3/\text{min}$, probably due to a change in the flow regime around the cell (Figure 2B). Higher flow rates seem to provide the highest oxygen concentration gradient across the cell.

The flow pattern is more complicated for the two configurations shown in Figure 1C and D. It can be seen that a relatively low flow rate is optimum when the gas mixture reaches first the cathode (where the oxygen partial pressure should be highest for maximum OCV), as concluded from the curves in Figure 2C. In fact, the OCV decreases for high flow rates ($>200 \text{ cm}^3/\text{min}$),

probably due to turbulence which increases mixing of the gases on both sides of the cell. Quite the opposite, flow rates higher than $200\text{cm}^3/\text{min}$ are necessary to produce similar OCV values when the gas mixture reaches the anode first, most likely due to consumption of the O_2 in partial oxidation reactions.

Propane/air ratio. All gas mixtures tested were rich in fuel and above the upper limit of the explosive range (9.5%). In general, it was found that the higher the $\text{O}_2:\text{C}_3\text{H}_8$ ratio, the higher the observed OCV. This is not surprising, as one would expect, due to higher O_2 concentration gradients generated with leaner fuel ratios (see Figure 2, A-D). However, the dependence of power density on fuel ratio did not always follow the same trend, as was the case of closed tube (Figure 3A) and open tube anode first (Figure 3D) configurations, probably due to higher gas mixing in these cases, at the relatively high flow rate used ($300\text{ cm}^3/\text{min}$). On the basis of these results, it can be predicted that higher $\text{O}_2:\text{C}_3\text{H}_8$ ratios, closer to the stoichiometric ratio of 5:1 (highest ratio tested here, 1.9:1, corresponds to 10% propane in air) would likely yield even better SCFC performance. However, such gas mixtures are explosive, and have to be diluted with inert gas to preserve the high $\text{O}_2:\text{C}_3\text{H}_8$ ratio, thus reducing the O_2 partial pressure. Further studies are necessary to evaluate the benefits/drawbacks of having high $\text{O}_2:\text{C}_3\text{H}_8$ ratios but lower O_2 partial pressure.

Power density performance. As noted by Bay et al.,⁹ the design of the test chamber for SCFCs has a significant effect on their performance parameters. Indeed, results of our systematic study, shown in Figure 3, A-D, confirm this observation, and provide new insight into the optimization of the chamber design. In the closed tube (A) and open tube anode first (D) configurations, the power density is lower than in the other two configurations due to increased mixing of the gases at the two electrodes, and, thus, decreased O_2 concentration gradient across the cell. Moreover, in neither case does the 10% propane-air mixture lead to the highest power density, even though the OCV is highest

for this gas composition. A plausible cause may be the partial consumption of fuel by electrochemical reactions at the electrodes, which has proportionally a larger effect in 10% gas mixture (the least rich).

In both of the other two configurations (open tube parallel, and open tube cathode first, Figure 3B, C) there is a monotonic increase of the power density with the $O_2:C_3H_8$ ratio, with the open tube parallel configuration providing the highest power density. However, it is likely that the cathode down configuration would lead to an even higher power density than all the other configurations at reduced flow rates ($150\text{ cm}^3/\text{min}$, for example), as inferred by the OCV data in Figure 2C.

Overall, the open tube anode first setup should be avoided, as it leads to lower OCV values, and even at higher flow rates its power density output is lower than the rest of the regimes tested.

Fuel efficiency. A parameter which may affect the attractiveness of SCFC for large scale applications is the fuel utilization. Implicit to the SCFC concept is the partial oxidation of the fuel by chemical reactions in the gas phase mixture. Moreover, the mixtures are rich in fuel, so a part of the fuel remains unreacted. All these limitations reduce the fuel efficiency to levels well below those of dual chamber SOFC, and increase even more the importance of the optimization of the flow rate, fuel/air ratio, and flow geometry.

Assuming that the only electroactive species at the anode is H_2 produced by the partial oxidation of propane, and that all O_2 in the gas mixture at the anode (half of the flow passes over anode) is used in this reaction, the fuel utilization can be calculated for each of the cases discussed in previous sections. For example, in the open tube geometry, the fuel utilization is less than 0.3%, with a maximum in fuel efficiency for about 0.2% fuel utilization at the flow rate of $300\text{ cm}^3/\text{min}$, as shown in Figure 4. While these figures are quite low compared to those currently reached in SOFCs,

the test system was not optimized for the best fuel utilization. Large amounts of gas mixture flow around the cell, without reacting at the electrodes, because of the large diameter of the test tube (1") compared to the diameter of the cell (1/2"), and half of the fuel passes over or around the cathode, designed to be inert to fuel reactions. Moreover, it is expected that some of the fuel will react by other reaction paths than the optimum one (partial oxidation), and some amounts of the produced H₂ will be oxidized in the gas phase instead of the electrode interface. Based on these arguments it can be assumed that the fuel efficiency of SCFC is significantly smaller than that of other SOFC, but the heat generated by gas phase oxidation reactions makes them the most suitable for self sustained power generation systems.

CONCLUSIONS

Four different test chamber configurations were tested with SCFCs, leading to very different performance parameters of the cells (OCV and power density) as a function of fuel/air ratio and total flow, most likely because they produce different gas compositions at the electrodes, and, thus, different $\Delta\mu_{O_2}$. The open tube parallel setup provides the highest power density if the total flow is relatively high (low fuel utilization), and the cathode first setup is best at higher fuel utilization (low total flow rate). Ideally, one would like to operate the cell in such conditions that $\mu_{O_2}(Anode) = 0$ due to partial oxidation reactions of the fuel at the anode, and the partial pressure of oxygen is as high as possible at the cathode. This work opens the prospect of SCFCs operated on dual gas supply, one rich in oxygen and fed to the cathode, and one rich in fuel and fed to the anode electrode, without complete separation of the two electrode chambers.

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REFERENCES

1. C. Eyraud, J. Lenoir, and M. Gery, *C.R. Acad. Sci. Paris*, **252**, 1599 (1961).
2. W. v. Gool, *Philips Res. Repts.*, **20**, 81 (1965).
3. T. Hibino, A. Hashimoto, T. Inoue, J. I. Tokuno, S. I. Yoshida, and M. Sano, *Science*, **288**, 2031 (2000).
4. T. Hibino, A. Hashimoto, M. Yano, M. Suzuki, S. Yoshida, and M. Sano, *J. Electrochem. Soc.*, **149**, A133 (2002).
5. Y. Shiratori and Y. Yamazaki, *Electrochemistry*, **69**, 92 (2001).
6. L. N. Van Rij, J. Le, R. C. Van Landschoot, and J. Schoonman, *J. Mater. Sci.*, **36**, 1069 (2001).
7. I. Riess, P. J. van der Put, and J. Schoonman, *Solid State Ion.*, **82**, 1 (1995).
8. T. Hibino, S. Wang, S. Kakimoto, and M. Sano, *Solid State Ion.*, **127**, 89 (2000).
9. L. Bay, T. Horita, N. Sakai, M. Ishikawa, K. Yamaji, and H. Yokokawa, *Solid State Ion.*, **115**, 363 (1998).
10. L. A. Chick, L. R. Pederson, G. D. Maupin, J. L. Bates, L. E. Thomas, and G. J. Exarhos, *Mater. Lett.*, **10**, 6 (1990).

LIST OF FIGURES

Figure 1. Single chamber fuel cell test configurations probing the effect of gas mixture flow in closed tube (A), open tube parallel (B), open tube cathode first (C), and open tube anode first (D) regimes.

Figure 2. Plots of OCV as a function of the flow rate of the propane-air gas mixture for SCFCs tested in the corresponding chamber configurations shown in Figure 1A-D at 600 °C, for different propane/air ratios: 10% - full circle, 12% - open circle, 14% - full triangle, 16% - open triangle.

Figure 3. Discharge curves of the SCFCs corresponding to the same experimental conditions specified in Figure 2 caption, for a flow rate of 300 cm³/min. The symbols correspond to the same propane/air ratios as before.

Figure 4. Fuel utilization vs. current density for a SCFC in the open tube parallel geometry, at a flow rate of 300 cm³/min.

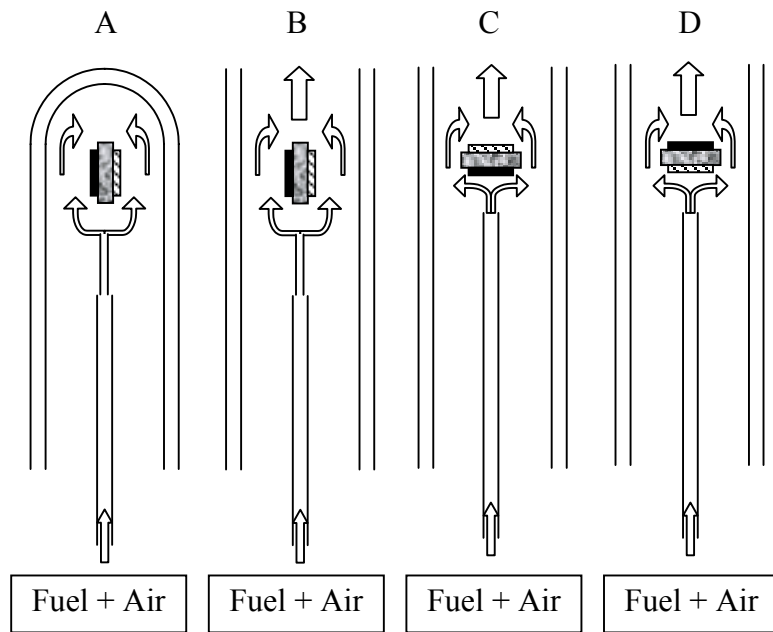


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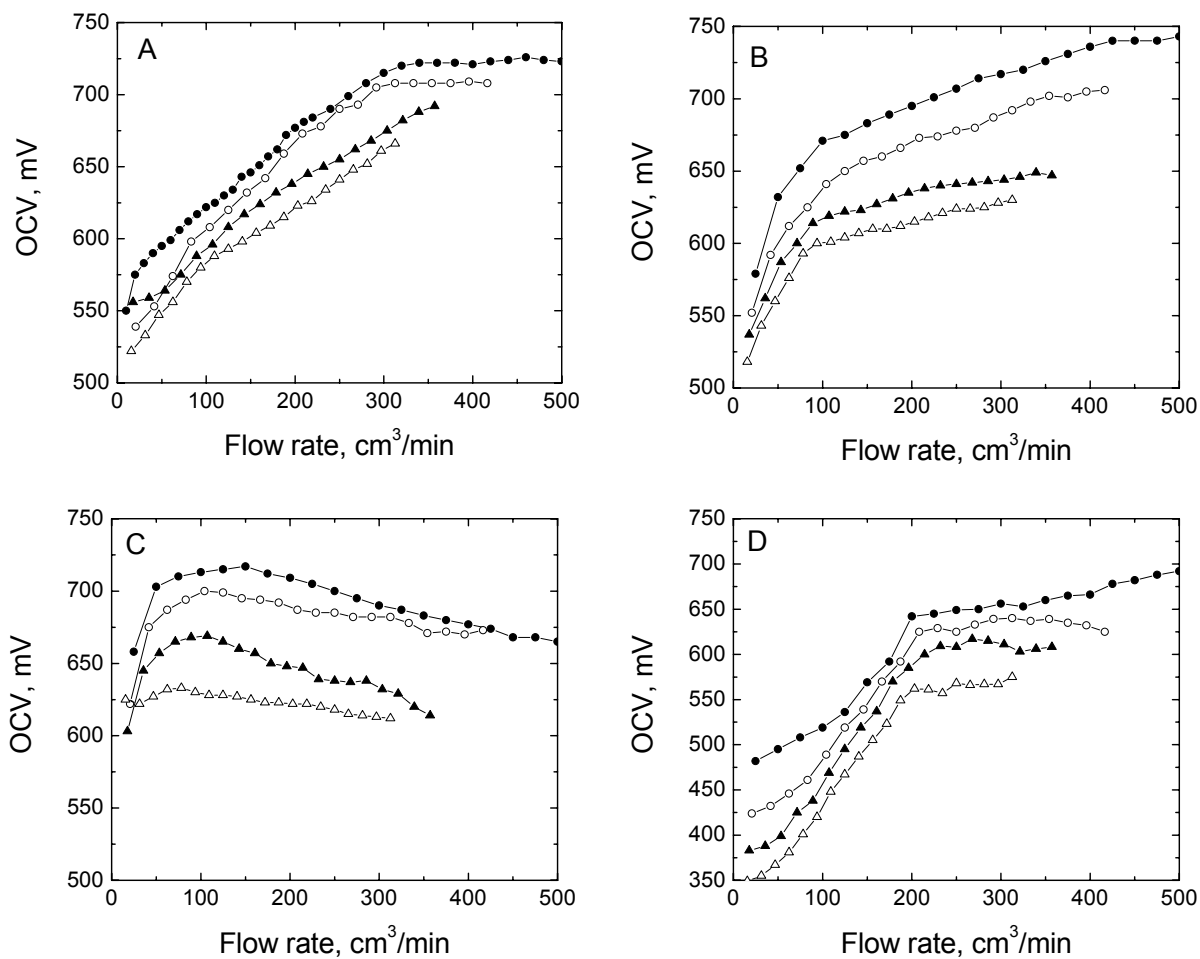


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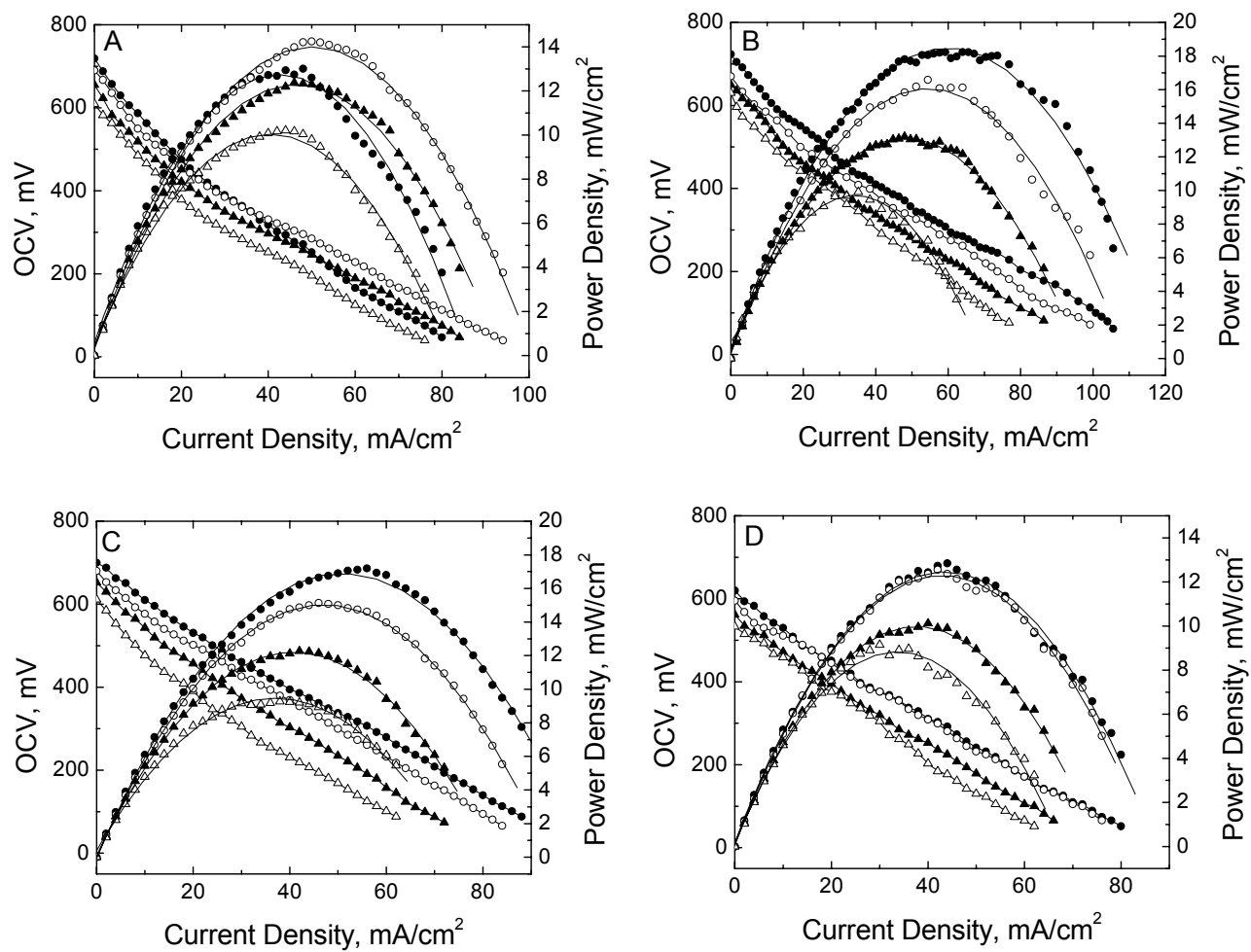


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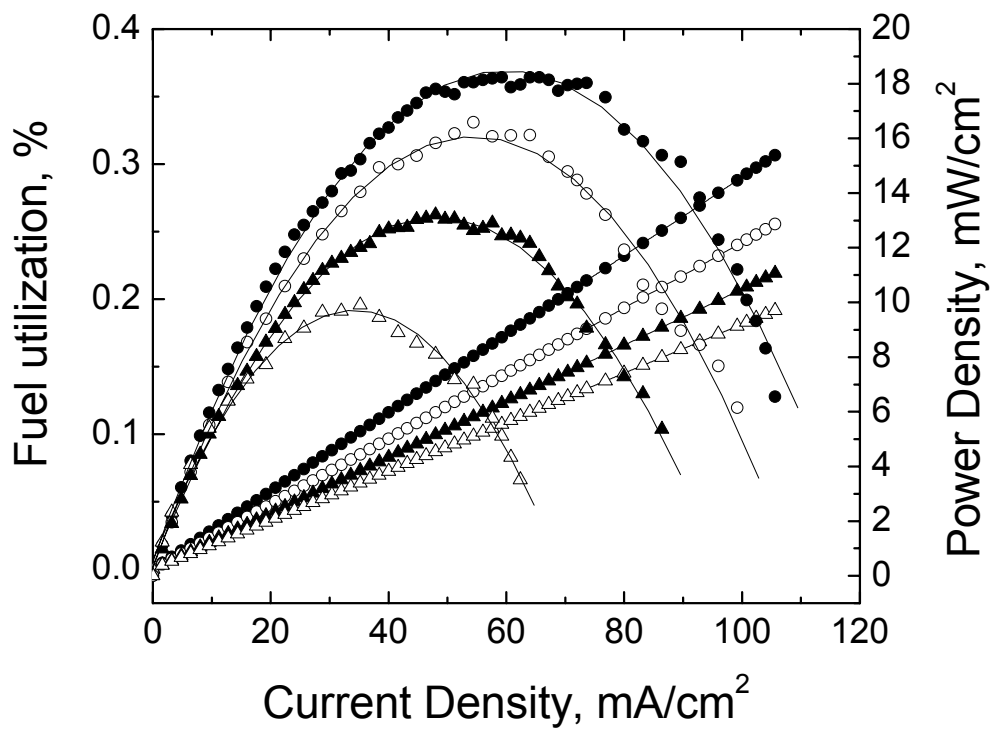


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