

Recent advances in direct methanol fuel cells at Los Alamos National Laboratory

Xiaoming Ren ^{*}, Piotr Zelenay, Sharon Thomas, John Davey, Shimshon Gottesfeld

Los Alamos National Laboratory, Los Alamos, NM 87545, USA

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Abstract

This paper describes recent advances in the science and technology of direct methanol fuel cells (DMFCs) made at Los Alamos National Laboratory (LANL). The effort on DMFCs at LANL includes work devoted to portable power applications, funded by the Defense Advanced Research Project Agency (DARPA), and work devoted to potential transport applications, funded by the US DOE. We describe recent results with a new type of DMFC stack hardware that allows to lower the pitch per cell to 2 mm while allowing low air flow and air pressure drops. Such stack technology lends itself to both portable power and potential transport applications. Power densities of 300 W/l and 1 kW/l seem achievable under conditions applicable to portable power and transport applications, respectively. DMFC power system analysis based on the performance of this stack, under conditions applying to transport applications (joint effort with U.C. Davis), has shown that, in terms of overall system efficiency and system packaging requirements, a power source for a passenger vehicle based on a DMFC could compete favorably with a hydrogen-fueled fuel cell system, as well as with fuel cell systems based on fuel processing on board. As part of more fundamental studies performed, we describe optimization of anode catalyst layers in terms of PtRu catalyst nature, loading and catalyst layer composition and structure. We specifically show that, optimized content of recast ionic conductor added to the catalyst layer is a sensitive function of the nature of the catalyst. Other elements of membrane/electrode assembly (MEA) optimization efforts are also described, highlighting our ability to resolve, to a large degree, a well-documented problem of polymer electrolyte DMFCs, namely “methanol crossover”. This was achieved by appropriate cell design, enabling fuel utilization as high as 90% in highly performing DMFCs. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Recent R&D efforts devoted to direct methanol fuel cells (DMFCs) have targeted potential applications ranging from portable power for consumer electronics to potential transport applications. At Los Alamos, we have been involved in DMFC R&D projects addressing potential applications covering this wide range. One central DMFC project at Los Alamos National Laboratory (LANL), funded by the Defense Advanced Research Project Agency (DARPA), has been devoted to portable power applications. The other has been devoted to potential transport applications and supported by the US DOE. Significant differences between technical parameters and targets for the two different DMFC applications we have addressed

include the lower cell temperature (60°C or below) and ambient air pressure preferred in portable power vs. operation around 100°C as target temperature, with possible use of pressurized air, for transport applications. Also, a much stronger concern for cost of catalyst and other stack materials and components arises in the context of DMFCs developed for potential transport applications.

Most, if not all recent DMFC work for either portable power or potential transport applications, has strongly focused on cells with polymeric, primarily perfluorocarbon sulfonic acid (PFSA) membrane electrolytes. In work at LANL, thin film catalysts bonded to the membrane, e.g., by a decal method [1] or, most recently mainly by direct application to the membrane, provided best results in terms of catalyst utilization and overall cell performance [2]. In earlier tests, our single DMFC hardware consisted of uncatalyzed carbon-cloth gas-diffusion backings and graphite blocks with machined serpentine flow channels — quite similar to hardware employed in work with hydrogen/air

^{*} Corresponding author.

PEFCs. Recently, the machined graphite hardware has been replaced by alternative, non-machined flow-field/bipolar plate hardware which enables effective air and aqueous methanol solution distribution along the cell active area at reduced cell width of just 2 mm.

2. Potential applications of DMFCs in portable power sources

Storage in liquid form is an important advantage of methanol vs. hydrogen for portable power source applications. The effective energy density of methanol, assuming DMFC cell voltage of 0.5 V (a typical design point) and 90% fuel efficiency, is 2.25 kW h/kg. In comparison, for hydrogen stored as metal hydride at 2% by weight and assuming hydrogen/air cell voltage of 0.7 V, the effective energy density of the fuel is 0.4 kW h/kg. As we show below, the power densities of a hydrogen/air PEFC and of a DMFC are not highly different when both operate near ambient conditions, leaving the DMFC system with the advantage of significantly denser form of (liquid) fuel storage.

2.1. DMFC short stack fabrication and testing

Our work, devoted to portable DMFC power sources, concentrated previously on core technology issues, particularly optimization of membrane/electrode assemblies (MEAs) for DMFCs and their fabrication, examination of the nature and extent of “methanol crossover” and possible solutions for it, and evaluation of other cell and stack materials and components. Most recently, we have moved, under DARPA sponsorship, to the fabrication of a small DMFC stack, to be incorporated by an industrial partner into a portable power system. This effort targets a 50 W/160 W h DMFC power source that could potentially replace the “BA5590” primary lithium battery, used by the US Army in communication systems. At this point, we have assembled, as an introductory step, a five-cell DMFC stack of 45 cm² active area, that utilizes the MEAs and hardware designed for the 50-W stack. Fig. 1 shows a photograph of the short stack assembled and tested at LANL and Fig. 2a and b show the performance of this short, five-cell DMFC stack tested first as hydrogen/air (Fig. 2a) and then as methanol/air (Fig. 2b) stack. Testing was performed under conditions relevant to portable power applications, i.e., the stack temperature was limited to 60°C and the (absolute) air pressure was 0.76 atm (corresponding to an elevation of 7500 ft at Los Alamos). As Fig. 2 shows, our short stack exhibited a ratio of maximum power densities better than 1:2 in operation on methanol/air vs. operation on hydrogen/air, under the conditions relevant to portable power applications. This result indicates that DMFC systems for portable power should compete favorably with systems based on hydro-

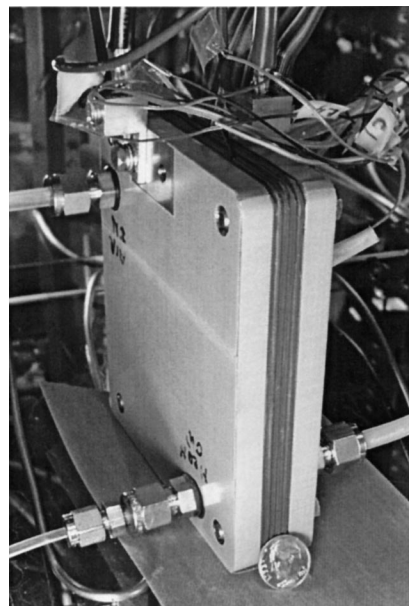


Fig. 1. Photograph of five-cell, short DMFC stack of 45 cm² active area, tested recently at LANL. Results of these tests are shown in Fig. 2 for stack operation under portable power conditions, and in Fig. 6 for stack operation under conditions relevant to transport applications.

gen/air PEFCs, particularly so for longer missions where the weight and volume of the fuel dominate. To estimate the energy density for a portable power system based on a DMFC, some assumptions on the volume and weight of water recirculation, heat rejection and air supply subsystems are required. Assuming that the weight of the auxiliaries is twice the weight of methanol fuel in a power system designed for 10 h of operation, system energy densities in excess of 200 W h/kg are projected [3]. At this level of energy density, DMFC power systems would compete favorably with advanced Li batteries, while providing the important advantage of ease of rechargeability.

An important feature of the DMFC stack technology developed by us recently (Figs. 1 and 2) is the narrow width (“pitch”) per cell of 1.8 mm, achieved while ensuring minimized pressure drop across the stack. The combined features of effective packaging and low transport losses are highly desirable in stack design. Parasitic power losses are lowered by minimizing pressure drop across the cell, as well as the stoichiometric flow of air. The latter is also quite critical to ensure that the cell could reach and maintain a design temperature with the simplest operation mode possible, i.e., using just a dry air blower for operation of the DMFC cathode. Our short stack has fulfilled well such combined requirements: on one hand, the tight packaging, at 1.8 mm per cell, has generated under such benign operation conditions an effective power density close to 300 W/l; also, thanks to a highly effective cathode flow field the stack could operate well with air stoichiometric flow rates as low as 2.5x–3.5x.

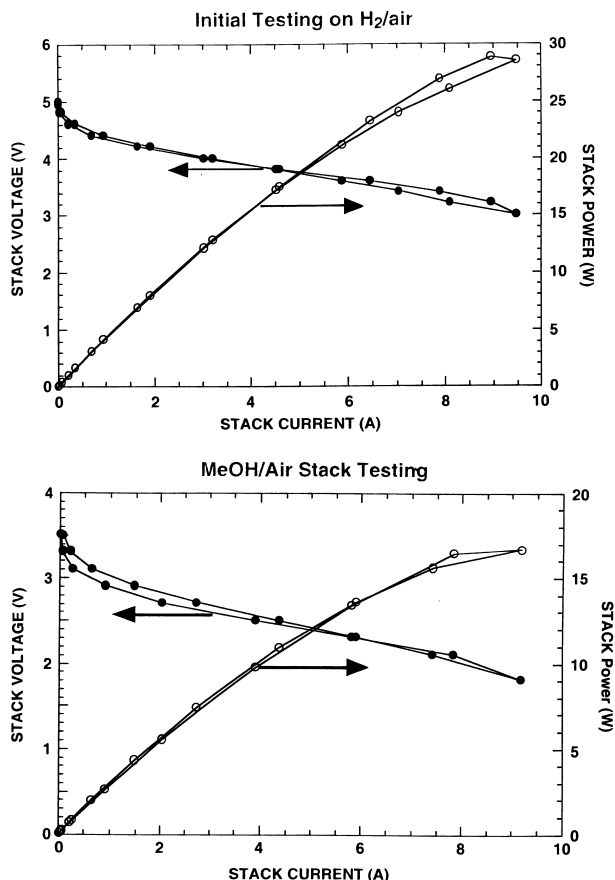


Fig. 2. Performance of five-cell DMFC stack operating (for reference) as hydrogen/air stack (a, top) and then as direct methanol/air stack (b, bottom). Maximum power density achieved in DMFC mode is seen to be over 50% of that achieved in H₂/air mode of operation of the same stack.

2.2. On methanol crossover

The effects of methanol crossover have been considered a severe barrier to faster development of DMFC technology. These effects consist of (i) lowering of methanol (fuel) utilization, resulting from fuel/oxygen recombination at the DMFC cathode catalyst, and (ii) the deleterious effects of methanol penetrating the cathode on the cathode performance. A central component of our recent DMFC cell and stack work, has been devoted to the definition of cell-design parameters required to lower the rate of methanol crossover in cells employing ordinary, i.e., quite “leaky” ionomeric membranes. The way to lower methanol crossover rate, in spite of the high permeability of methanol in the membranes available at present, is to lower the methanol concentration gradient within the cell that determines methanol flux under steady state operation conditions. Obviously, this goal has to be achieved without limiting cell performance in the process. Fig. 3 demonstrates the two tools available to achieve the required result: lower methanol feed concentration and optimized cell design. The former tool is obvious: with lowering of

the methanol feed concentration, the rate of crossover drops proportionately at zero cell current. The latter tool is more subtle: by using appropriate cell design, a significant drop in methanol crossover can be achieved with increase in cell current, i.e., with increase in rate of anodic consumption of methanol. Fig. 3 depicts the variation of crossover rate with cell current density, as measured (points) and as modeled (curves), based on independently derived cell parameters. Once such strong lowering of crossover (Fig. 3) is achieved, the remaining important question is whether the lowering of the methanol feed concentration and the use of such cell structure does not hurt cell performance. In other words, can high cell performance and lowered crossover losses be achieved simultaneously in a DMFC based on ordinary ionomeric membrane? The answer is shown in Fig. 4, that depicts together DMFC stack performance (current density at 0.45 V) and fuel utilization [= (cell current)/(cell current + crossover current)], measured at 60°C and ambient air pressure at 3x stoichiometric flow. Fig. 4 shows that, with such optimized cell structures, the required combination of high cell performance (close to 0.2 A/cm² at 0.45 V) and high fuel utilization (> 90%) can be achieved, in spite of the rather “leaky” membrane employed. This is an important result. It means that significant overall energy conversion efficiencies can be achieved in DMFCs, even before advanced membranes of much lower methanol permeability (and high protonic conductivity) are demonstrated in a compelling way. For example, operation at 0.5 V (typical design point) and 90% fuel utilization, amounts to an overall conversion efficiency, methanol-to-dc power, of 37%. As to cathode performance penalties, Fig. 5 shows detailed experimental evaluation of such losses in one of our single-cell DMFCs employing a Pt catalyst at the air cathode. In this case, measured at 80°C and with pressurized air, one can observe the polarization curve expected

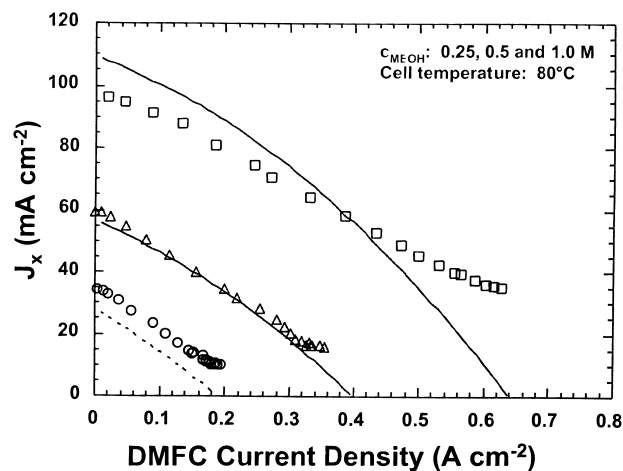


Fig. 3. Dependence of rate of methanol crossover, expressed in terms of equivalent current density (J_x), measured for a DMFC using three methanol feed concentrations and cell design that drops the rate of crossover significantly with cell current.

after (i) correcting for iR losses and (ii) correcting also for the crossover losses in the cathode based on measured rate of methanol crossover as function of cell current (lower curve) and assuming additive currents (of opposite sign) of methanol oxidation and oxygen reduction at the cathode catalyst [4]. It can be seen that cathode losses caused by crossover (with the 1 M methanol feed employed here) are so close to 50 mV at 100 mA/cm², dropping below 20 mV at 200 mA/cm² and practically vanishing at 300 mA/cm².

Water management remains a relatively demanding requirement in such a portable, liquid-fed DMFC power system, originating from the need to supply the anode with aqueous solution of methanol of concentration not exceeding 1 molar (1 M), in order to minimize crossover. Fortunately, intrinsic DMFC anode activity is not affected by lowered methanol feed concentration down to the 0.1 M level, as the electrocatalytic process at the PtRu catalyst is zero order in methanol in this concentration range. However, the continuous flow of water from anode to cathode when the DMFC is under current, taking place by electro-

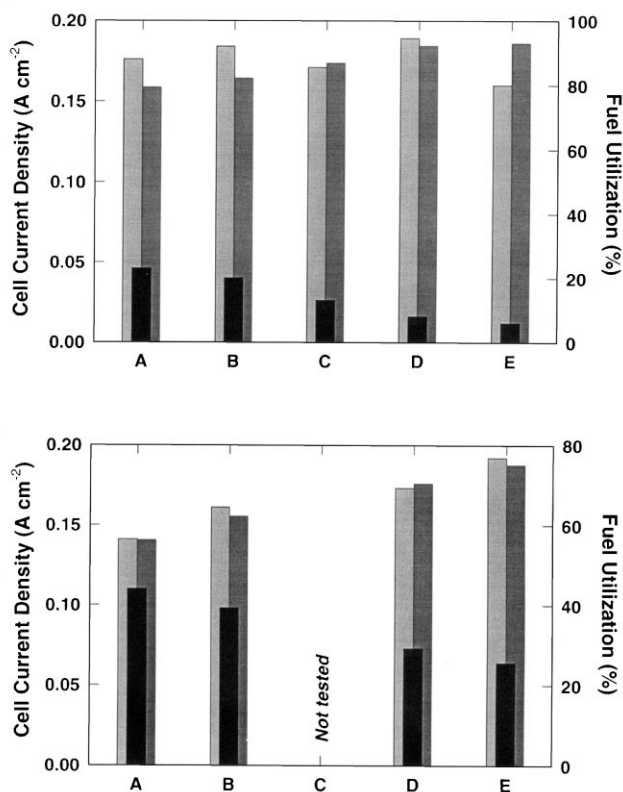


Fig. 4. Use of combinations of direct methanol/ambient air cell components and operation conditions, to achieve simultaneously high cell performance and high fuel utilization (cell operation at 0.45 V, 60°C). Examples A to E correspond to five different cell structures. Top figure corresponds to 0.5 M methanol feed stream and bottom figure to 1.0 M. Light gray bars correspond to cell current density at 0.45 V (left axis), black bars to rate of crossover in terms of current density (left axis) and dark gray bars to fuel utilization (right axis). Case d in top figure shows best combination: 0.18 A/cm² at 0.45 V and >90% fuel utilization.

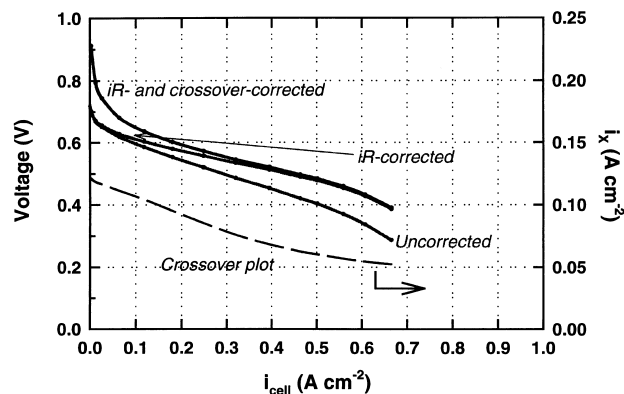


Fig. 5. Experimental evaluation of DMFC cathode voltage loss incurred by methanol crossover when Pt catalyst is employed. The evaluation is based on the measured rate of crossover as function of cell current density and the assumption that methanol oxidation and oxygen reduction currents at the cathode are additive, with no further effect of methanol on cathode performance (80°C, 1 M MeOH, 30 psig air).

osmotic drag at the rate of 2.5–3 H₂O/H⁺ near 60°C [5], requires to return liquid water from the cathode exhaust to the anode compartment to retain the dilute methanol anode feed composition (unless methanol is stored as dilute aqueous solution at a significant penalty in energy density). However, it seems that this challenge at the DMFC system level can be relatively easily answered, using a neat methanol source and a methanol concentration sensor to keep the anode feed concentration at the level required.

In summary, DMFC-based portable power systems have good potential to compete favorably with hydrogen-fueled equivalents. Not only is liquid fuel of high energy density an obvious advantage, it is the ability to reach DMFC power densities of the order of 300 W/l of active stack volume under mild operation conditions that makes such systems attractive targets for further development. Furthermore, fuel utilization can be improved with proper cell design up to the level of 80–90%, in spite of the relatively “leaky” (but well-conducting) membranes employed to date. The technology of DMFC-based portable power systems is at a stage where complete power systems need to be demonstrated providing answers within the small volumes targeted for all relevant mass and heat transport requirements.

3. DMFCs as potential power sources for transport applications

The objective of our direct methanol fuel cell effort sponsored by DOE/OAAT, has been to develop materials, components and operation conditions for such cells and small stacks, that would prove their potential for transport applications in terms of power density, energy conversion efficiency and cost. A DMFC as primary power source for transport has the potential to achieve the combined attrac-

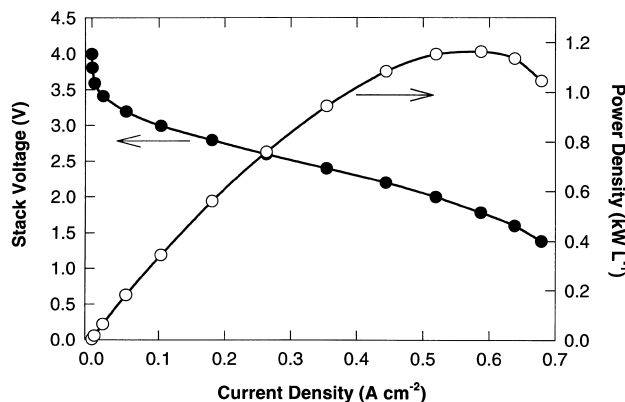


Fig. 6. Five-cell DMFC stack performance at 100°C on 1 M methanol/30 psig air.

tive properties of a liquid fuel of good potential availability, high system simplicity (liquid fuel + air *in*, dc power *out*), good potential for packaging as required to achieve 350-mile range in a passenger vehicle, and a good potential for ZEV characteristics.

Our approach in working on potential transport applications of DMFCs has been based on raising the DMFC temperature to around 100°C, to achieve competitive power densities [6]. We have targeted a power density of the order of 1 kW/l, as achieved in PEMFC stacks operating on methanol reformat. In our most recent work, we have focused on first demonstration of operation near 100°C of the DMFC short stack based on LANL stack hardware (Fig. 1), operating on aqueous methanol and pressurized (30 psig) air. As described above, the five-cell stack (of 45 cm² active area) had a pitch of only 2 mm per cell, allowing, at the same time, operation with pressure drops across the stack as low as 1 in. of water. Fig. 6 demonstrates the performance achieved from that five-cell stack under conditions that may be relevant to transport applications, in terms of voltage–current and power–current characteristics. Maximum power density generated by the stack under these conditions was 50 W. The active part of the stack volume was 45 cm³, thus maximum power density was 1.1 W/cm³, or 1 kW/l. This is certainly a respectable level of power density, reaching a similar order as achieved from reformat/air PEM fuel cell stacks.

For operation of this stack at 100°C, we measured, by detailed mass balance, methanol utilization rate of 82% with an anode feed of 1 M methanol and as high as 99% (with error bar of around 5%) when the methanol feed concentration was lowered to 0.75 M. This high fuel utilization was again achieved by optimizing electrode structure, rather than by any significant membrane modification. High fuel utilization can thus be reached in DMFC stacks today together with the power densities relevant to transport applications. As our results have shown, this can be done even before the (highly desirable) development of advanced membranes of lower methanol crossover and

high protonic conductivity takes place. This conclusion could be of significance regarding the potential time line for demonstration and implementation of DMFC technology in transport, where energy conversion efficiency is of prime significance.

Finally, to address the important issue of cost, we have recently pursued further the target of lowering catalyst loadings in DMFCs while maintaining performance. Fig. 7 illustrates DMFC results obtained near 100°C with relatively lower loadings of Pt. To achieve better catalyst utilization, we returned to work with carbon-supported PtRu anode catalysts, after having invested most previous effort in optimizing the performance of unsupported PtRu catalysts. The highest effective catalyst activity demonstrated, was 5 mg Pt/W (or 5 g Pt/kW), counting total loading in the DMFC, i.e., anode + cathode Pt loading. This amounted to a factor of two improvement over catalyst activity in DMFCs we demonstrated to date and provided a further significant step in lowering DMFC catalyst cost — a critical requirement in transport applications. The state-of-the-art catalyst technology for direct and indirect methanol fuel cell systems can be roughly

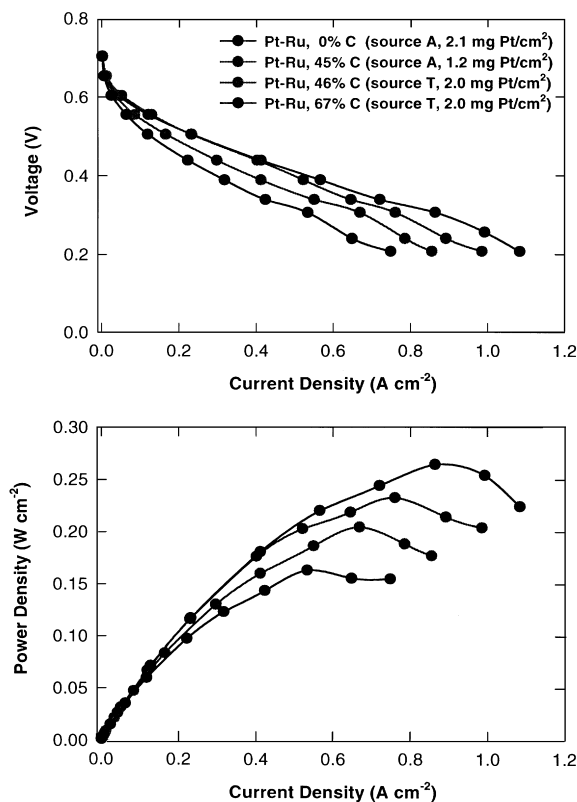


Fig. 7. Voltage–current (top) and power–current (bottom) plots for DMFCs employing lower precious metal loading. The curves correspond to four samples of PtRu/C anode catalysts used in MEA preparation, designated in the upper corner. The Pt loading designated in each case in total loading for both sides of the MEA. The order of the curves, top to bottom, is the same as the printed order of the four samples. The second sample shown generated 0.246 W/cm² with 1.2 mg/cm², i.e., 4.9 mg/W (or 5 g/kW).

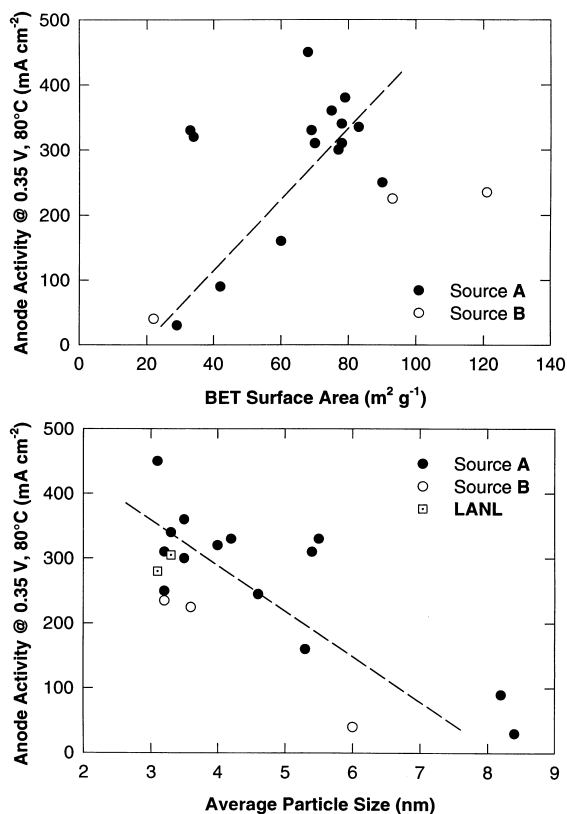


Fig. 8. Performance of 19 different samples of unsupported PtRu catalysts from three different sources, as DMFC anode catalysts. MEAs were prepared by application of the catalysts to one side of a Nafion® 117 membrane. Anode activity was measured at 0.35 V vs. an H₂ evolving cathode, utilizing a Pt catalyst layer on the other side of the MEA.

described as a ratio of 2.5:1 between DMFC stack and (overall system) reformate/air precious metal loadings demonstrated per kilowatt. While certainly significant and a future target for further effort, this gap is smaller than usually perceived.

In summary, as a result of these efforts at LANL targeting potential transport applications of DMFCs, the technical status advanced quite significantly. In terms of power density and energy-conversion efficiency, the DMFC (based on short-stack results) is today comparable with the on-board methanol reforming system. There is a remaining (although smaller than perceived) gap in precious metal catalyst requirements, with the DMFC requiring 5 g Pt kW⁻¹ vs. about 2 g Pt kW⁻¹ required today for an on-board reforming system. This gap could be closed further by optimization for higher temperature cell operation and further anode catalyst work. DMFC power system analysis, based on the performance of our stack, under conditions applying to transport applications has shown (joint effort with U.C. Davis) that, in terms of overall system efficiency and system packaging requirements, a power source for a passenger vehicle based on a DMFC could indeed compete favorably with a hydrogen-fueled fuel cell system, as well as with fuel cell systems based on fuel processing on board.

4. The DMFC anode catalyst

There is little doubt that improved anode catalytic activity is the one most important target that needs to be achieved before DMFCs could see the highly desirable further improvements in energy conversion efficiency and lowered cost. We have devoted significant effort to screening of a wide range of “unsupported” PtRu catalysts, based on the optimized application of thin film catalyst layers to ionomeric membranes [2]. In the process, we have found that this optimization could be a very sensitive function of catalyst composition. For example, in some samples of unsupported PtRu catalysts, we discovered that best performance was obtained with the thinnest and densest catalyst layers prepared with no addition of recast ionomer [7]. Apparently, anhydrous Ru oxide component could provide sufficient protonic conductivity in such catalyst layers [7]. Having optimized application to membrane for several different catalyst samples, we have found large variability in the activity of unsupported PtRu samples of formal composition close to 1:1 (atomic ratio) as DMFC anode catalysts. Fig. 8 summarizes measurements for a significant number of such PtRu catalyst samples, made by us into MEAs. It shows the obvious advantage of smaller particle size (higher catalyst surface area), but also clarifies that particle size is far from being the only important factor.

Acknowledgements

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References

- [1] S. Gottesfeld (with T. Zawodzinski), Polymer electrolyte fuel cells, in: C. Tobias, H. Gerischer, D. Kolb, R. Alkire (Eds.), *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 5, Wiley/VCH, 1997.
- [2] X. Ren, M.S. Wilson, S. Gottesfeld, *J. Electrochem. Soc.* 143 (1996) L12–L15.
- [3] S. Gottesfeld, M.S. Wilson, Polymer electrolyte fuel cells as potential power sources for portable electronic device, in: T. Osaka, M. Datta (Ed.), *Energy Storage Systems for Electronics*, International Publishers Distributor (S), in press.
- [4] D. Chu, S. Gilman, *J. Electrochem. Soc.* 141 (1994) 1770.
- [5] X. Ren, W. Henderson, S. Gottesfeld, *J. Electrochem. Soc.* (1997) L267–L269.
- [6] X. Ren, M.S. Wilson, S. Gottesfeld, in: S. Gottesfeld, G. Halpert, A. Landgrebe (Eds.), *Proton Conducting Membrane Fuel Cells I*, The Electrochemical Society, Pennington, NJ, Oct. 95, pp. 252–260.
- [7] S. Thomas, X. Ren, S. Gottesfeld, *J. Electrochem. Soc.*, in press.