

Triode fuel cells

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Abstract

The triode fuel concept is discussed together with some of its first applications in the areas of SOFCs and PEMFCs. It is shown that, when the electrodes are polarizable, both the power output and the thermodynamic efficiency can be improved quite significantly via application of electrolytic currents between the anode or cathode and an auxiliary electrode.

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1. Introduction

A new device and method is described for enhancing the power output and thermodynamic efficiency of batteries and fuel cells [1,2]. In addition to the anode and cathode, the new device introduces a third electrode together with an auxiliary circuit which is run in the electrolytic mode and permits fuel cell operation under previously inaccessible anode–cathode potential differences [3,4]. The new device and method introduces a new controllable variable in fuel cell operation, i.e. the potential or current applied between the anode or cathode and the counter electrode (Fig. 1A). The concept of the triode fuel cell operation has been validated and tested using a solid oxide fuel cell (SOFC) employing polarizable Pt paste electrodes [3]. The triode concept is also demonstrated here with state-of-the-art PEMFC units, showing significant enhancement of the overall cell performance. A similar three-electrode arrangement has been used to diminish the impedance of Au electrode deposited on YSZ [5].

As shown in Fig. 1A, the system contains three electrodes: the anode, which also serves simultaneously as the working electrode (W) of the auxiliary electrochemical cell, the cathode and the counter electrode of the auxiliary electrochemical cell.

The three electrodes are all in electrolytic contact and form two electrical circuits:

- the fuel cell circuit which comprises the anode, the cathode and a variable resistance, R_{EX} , for dissipating the electrical power, P_{fc} , produced.
- the auxiliary circuit which comprises the working electrode (same as the anode or cathode of the fuel cell), the counter electrode and a galvanostat or potentiostat.

When the imposed auxiliary current, I_{aux} , is zero, then the fuel cell operates in the conventional mode (open auxiliary circuit), while $I_{aux} \neq 0$ corresponds to triode operation.

2. Experimental

As shown in Fig. 1B, and described in detail elsewhere [3], the three Pt electrodes of the triode SOFC system were deposited on the solid electrolyte, an YSZ (8 mol% Y_2O_3 -stabilized- ZrO_2) tube closed flat at one end. The anode electrode deposited on the inside of the YSZ tube bottom had a superficial area of 2 cm^2 and thickness $3\ \mu\text{m}$, while the cathode, a similarly deposited Pt film of ring shape at the periphery of the outside surface of the bottom wall of the YSZ tube (Fig. 1B), had a surface area of 1 cm^2 . The counter electrode was a circular dot Pt electrode of area 0.33 cm^2 deposited around the center of the same outer surface. For the experiments we have used a variety of fuels, i.e. dry H_2 , ethane and methane at temperatures 400 to

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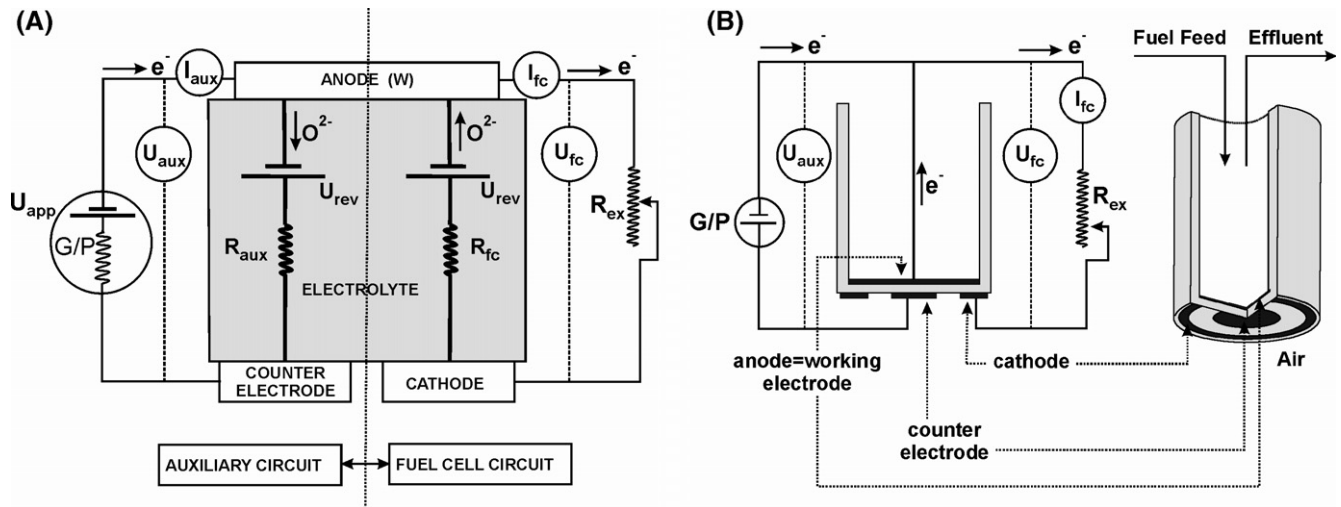


Fig. 1. Schematic of the triode fuel cell concept. The fuel cell anode acts simultaneously as the working electrode of the auxiliary circuit; G/P: galvanostat–potentiostat. (B) Experimental triode solid oxide fuel cell (SOFC) showing the location of the Pt anode, cathode and counter electrodes on the closed-flat at one end Y_2O_3 -stabilized- ZrO_2 (YSZ) tube.

750 °C. The fuel was supplied continuously at the anode with the cathode exposed to ambient air for the supply of O_2 .

The PEM fuel cell used in the present work, shown schematically in Fig. 2A, was obtained from NuVant and is identical to the one described in several previous studies [6–8]. This cell has been properly modified in order to operate as a triode PEM (Fig. 2B). The cathode metal loading was 4 mg Pt/cm² (unsupported Pt black) on E-TEK carbon cloth. The anode was Pt (30%) Ru(15%) supported on Vulcan XC-72 carbon deposited by NuVant [7,8] on E-TEK carbon cloth (4 mg/cm², thus 1.8 mg/cm² metal basis). The three electrode geometric surfaces were: Anode electrode: 3.02 cm², auxiliary electrode: 2.27 cm² (on the same side with anode), cathode electrode: 5.29 cm².

The anode and cathode feeds were continuously humidified using thermostated gas saturators. The cell temperature was typically set at 30 °C and the gas saturators at around 40 °C. The anode gas was H_2 , CO mixtures diluted with He or a Messer–

Griesheim certified mixture of 33.7% H_2 , 33.7% CO_2 , 0.63% CO in N_2 , while the cathode feed was humidified Air Liquide synthetic air (20% O_2 in N_2).

The triode fuel cell operation consists of imposing an electrolytic current, $I_{aux} \neq 0$, or potential to the auxiliary system. Denoting by I_{far} the net Faradaic fuel-consuming current, it is noted that in view of Figs. 1A and 2B and Kirchhoff's first Law it is:

$$I_{fc} = I_{aux} + I_{far} \quad (1)$$

where I_{fc} is the current in the fuel cell circuit.

3. Results and discussion

3.1. Proof of concept with solid oxide fuel cell

Fig. 3 demonstrates the triode principle for a solid oxide fuel cell with polarizable, i.e. high impedance, Pt electrodes,

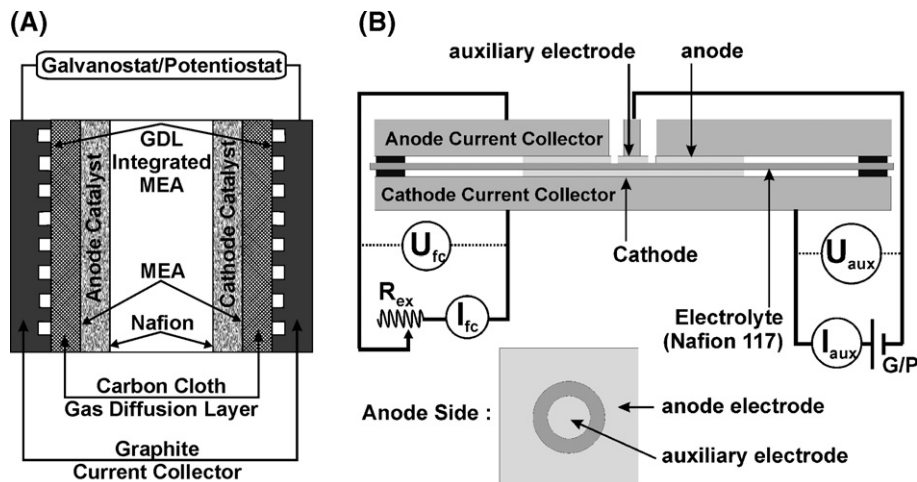


Fig. 2. (A) Schematic of the state-of-the-art PEMFC unit: geometry and basic electrical circuit. (B) Schematic of the triode PEMFC showing the membrane electrode assembly (MEA) and the electrical circuits between the anode, the cathode and the auxiliary electrodes.

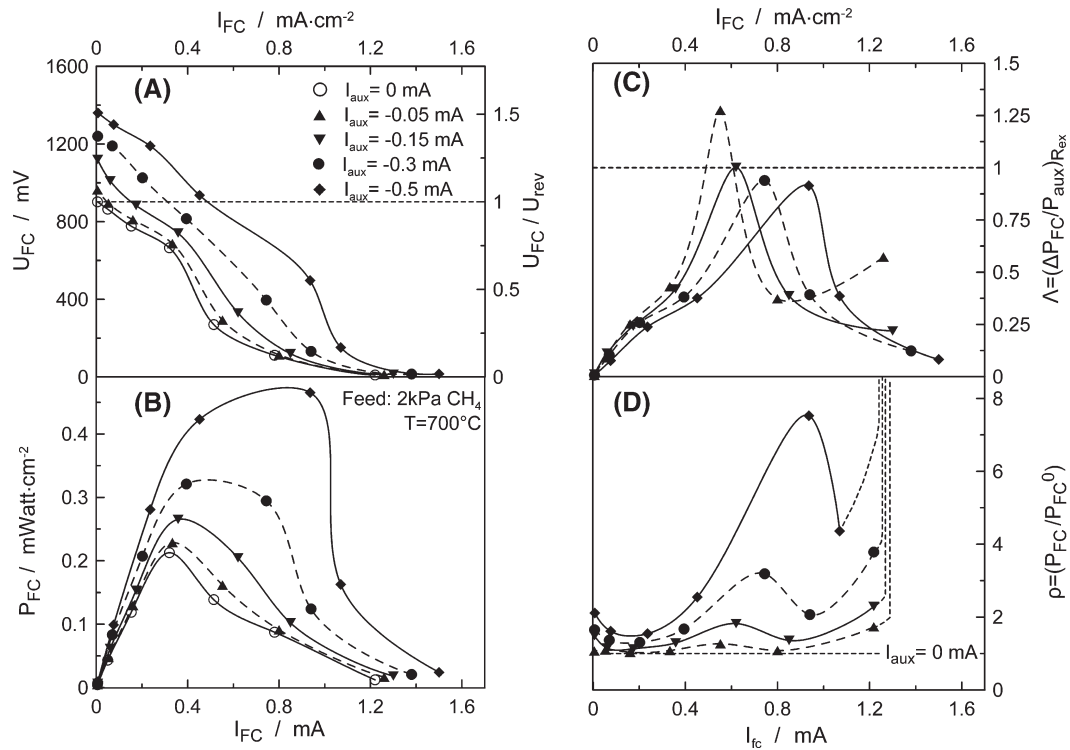


Fig. 3. Triode solid oxide fuel cell operation: effect of fuel cell current (A) on the operating fuel cell potential, U_{FC} , and U_{FC}/U_{rev} ratio, (B) on the fuel cell power density, (C) on the power gain ratio $A (= \Delta P_{FC}/P_{aux})$ and (D) on the power enhancement ratio $\rho (= P_{FC}/P_{FC}^0)$, when electrolytic currents (0.05–0.5 mA) are applied to the auxiliary circuit. $T_{cell} = 700^\circ\text{C}$, feed: 2kPa CH_4 in He at 180cc STP/min.

which limits the power output to very low values, supplied with 2% dry CH_4 in the anode feed (balance He) at 700°C . It can be seen that the open-circuit ($I_{FC} = 0$) anode–cathode potential difference during triode SOFC operation is increased by imposing various electrolytic currents, I_{aux} , in the auxiliary circuit. It reaches values up to 1.4 V, well above the reversible potential, U_{rev} , at the normal SOFC operation ($I_{aux} = 0$). The corresponding power output of the cell is enhanced by up to a factor of eight, i.e. the power enhancement ratio $\rho (= P_{FC}/P_{FC}^0)$ [3] equals eight (Fig. 3D). The power gain ratio, A , has been defined [3] as $A = \Delta P_{FC}/P_{aux}$, where ΔP_{FC} is the change (gain) in the power output of the fuel cell due to the operation of the auxiliary circuit and P_{aux} is the power consumed in the auxiliary circuit [3]. As shown in Fig. 3, triode operation leads to a significant enhancement in the power output of the cell (Fig. 3D) and under some conditions it also leads to an enhancement in the overall thermodynamic efficiency (Fig. 3C), i.e. the increase in the power output of the SOFC is higher than the power sacrificed in the electrolytic circuit as depicted in Fig. 3C.

This significant enhancement of SOFC performance is due to the establishment of a mixed potential at the anode (or the cathode) of the cell, which is dictated and controlled by the auxiliary circuit overpotential [3]. This corrosion-type [9] potential, diminishes the impedance between anode and cathode [5] and leads to a decrease in anodic and cathodic overpotential, due to the enhancement of the overall rate of anodic oxidation which is normally limited by the supply and adsorption of the fuel at the anode [1,10]. Thus the triode fuel

cell operation is quite advantageous under high Wagner number conditions, i.e. when the anodic or cathodic overpotential is significantly higher than the ohmic losses. It should be noted that the main reason for the very pronounced power output enhancement observed here is the very low initial power output of the cell and the very high polarizability of the Pt paste electrodes. Work is currently in progress to test the triode operation of state-of-the-art SOFC units [11].

3.2. Demonstration of triode concept with a state-of-the-art PEM fuel cell

The triode fuel cell design and operation can be advantageous for enhancing the performance of CO poisoned anodes of state-of-the-art PEM fuel cell units, where inefficient electrocatalysis at the anode or the cathode of the cell creates significant overpotential losses. In this work we studied the performance of a state-of-the-art PEM fuel cell unit (Fig. 2A), obtained from NuVant Systems Inc., which we have properly modified in order to operate it as a triode fuel cell (Fig. 2B) [6].

Fig. 4 shows the effect of triode operation in a PEM fuel cell where the anode is poisoned by CO ($P_{CO} = 100\text{ppm}$) and compares it with normal operation ($I_{aux} = 0$) when only H_2 is present at the anode (open circles). As shown in Fig. 4A and B, increasing auxiliary current I_{aux} causes a pronounced increase in the operating fuel cell potential (Fig. 4A) and power output (Fig. 4B). For low and intermediate currents,

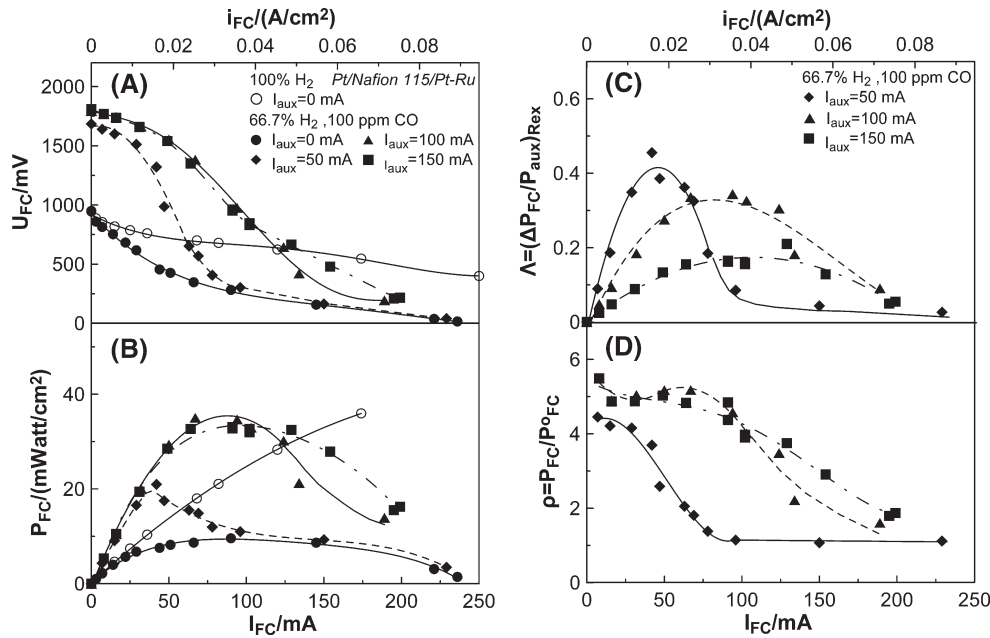


Fig. 4. Current–potential (A), current–power output (B), current–power gain ratio, Λ , (C) and current–power enhancement ratio ρ (D) curves for a CO-poisoned anode PEMFC (filled symbols) at various auxiliary currents and comparison with cell performance in pure H₂ (open circles).

triode operation leads to higher fuel cell potential and power output not only than those of the CO poisoned cell (filled circles) but also higher than those of the cell operating with pure H₂ (open circles).

Figs. 4C and D show the corresponding effect of current on the power enhancement ratio ρ ($=P_{fc}/P_{fc}^0$) and the power gain parameter Λ ($=\Delta P_{fc}/P_{aux}$). The former takes values up to 5, i.e. there is a 500% power output enhancement, but the latter is below unity ($\Lambda < 1$), i.e. the overall system thermodynamic efficiency is decreased.

An example where $\Lambda > 1$, and thus the overall thermodynamic efficiency is enhanced, is shown in Fig. 5. In this case the anode is fed with an H₂O saturated gas mixture containing 4.6% H₂, 4.05% CO₂, and 760 ppm CO. Application of auxiliary currents causes an enhancement in the operating potential for all

values of the Faradaic current I_{far} (Fig. 5A) and thus Λ takes values well above unity, i.e. up to five (Fig. 5B). Under these conditions the overall system thermodynamic efficiency is enhanced, i.e. more power is gained in the fuel cell circuit than that sacrificed in the auxiliary circuit.

The pronounced effect of triode operation in the performance of CO poisoned PEM fuel cells is a primarily due to the fact that protons supplied by the auxiliary electrode to the anode decrease significantly the coverage of adsorbed CO. An additional factor is the enhanced conductivity of the Nafion membrane due to the additional pumping of protons in the membrane during triode operation [6,12,13]. This has been shown to be the main enhancement mechanism under conditions where the anodic overpotential is negligible [6].

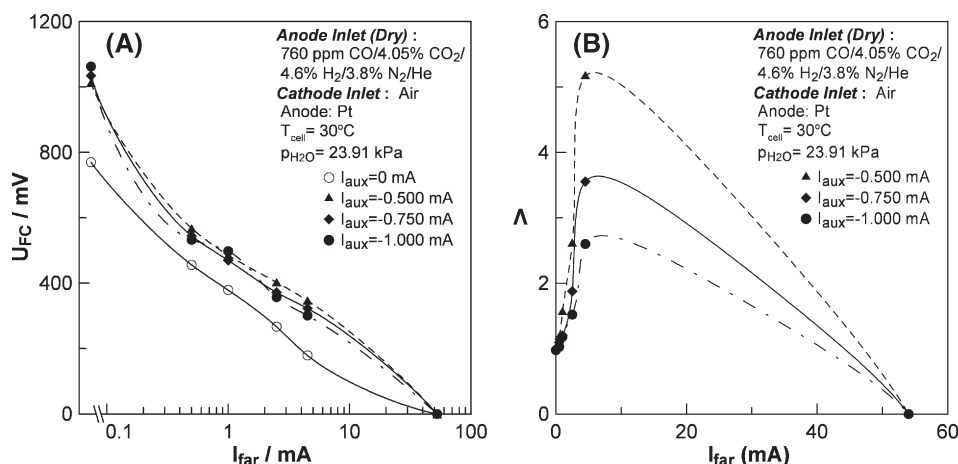


Fig. 5. Effect of auxiliary current and net Faradaic current on the fuel cell potential (A) and power gain ratio, Λ , (B) for a PEMFC unit operating with a mixture containing 760 ppm CO, 4.05 kPa CO₂ and 4.6 kPa H₂.

4. Conclusions

When the electrode impedance is high, the triode operation of fuel cells results in a significant enhancement of their operating potential (up to 2 V) and power output (up to a factor of 8). Under certain operating conditions, the overall thermodynamic efficiency is also enhanced. The triode operating mode, which conceptually resembles a continuous “recharging” of a battery or fuel cell during actual operation, is advantageous under conditions of high anodic and cathodic overpotential. Application of the triode concept to low-temperature SOFC and CO-poisoned PEM fuel cell units can decrease electrode polarization losses and may, in principle, permit the use of alternative less costly electrode materials.

References

- [1] W. Vielstich, A. Lamm, H. Gasteiger (Eds.), *Handbook of Fuel Cells: Fundamentals, Technology and Applications*, vol. 2, John Wiley & Sons Ltd., New York, 2003.
- [2] S.C. Singhal, *Solid State Ionics* 135 (2000) 305.
- [3] S.P. Balomenou, C.G. Vayenas, *J. Electrochem. Soc.* 151 (2004) A1874.
- [4] S. Balomenou, C.G. Vayenas, WO 2005/008820 (2005).
- [5] A. Hashibon, S. Raz, I. Riess, *Solid State Ionics* 149 (2002) 167.
- [6] A. Katsaounis, S. Balomenou, D. Tsipalakes, S. Brosda, S. Neophytides, C.G. Vayenas, *Appl. Catal., B Environ.* 56 (2004) 251.
- [7] R. Liu, E.S. Smotkin, *J. Electroanal. Chem.* 535 (2002) 49.
- [8] B. Gurau, E.S. Smotkin, *J. Power Sources* 112 (2002) 339.
- [9] J.O.M. Bockris, A.K.M. Reddy, M.E. Gamboa-Aldeco, *Modern Electrochemistry*, vol. 2A, Kluwer Academic/Plenum Publishers, New York, 2001.
- [10] C.G. Vayenas, S. Bebelis, C. Pliangos, S. Brosda, D. Tsipalakes, *Electrochemical Activation of Catalysis: Promotion, Electrochemical Promotion and Metal–Support Interactions*, Kluwer Academic/Plenum Publishers, New York, 2001.
- [11] F. Tietz, D. Presvytes, S.P. Balomenou, C.G. Vayenas, (in preparation).
- [12] A. Katsaounis, S. Balomenou, D. Tsipalakes, M. Tsampas, C.G. Vayenas, *Electrochim. Acta* 50 (2005) 5132.
- [13] M. Tsampas, A. Picos, S. Brosda, A. Katsaounis, C.G. Vayenas, *Electrochim. Acta* 51 (2006) 2743.