Electronic Supporting information

Direct formate anion exchange membrane fuel cells with a PdAu bimetallic nanoparticle anode electrocatalyst obtained by metal vapor synthesis.

Carolina Castello,[1,2] Tailor Peruzzolo,[1*] Marco Bellini,[1] Maria V. Pagliaro,[1] Francesco Bartoli,[1] Enrico Berretti,[1] Lorenzo Poggini,[1,3] Emanuela Pitzalis,[4] Claudio Evangelisti,[4*] Hamish A. Miller[1*]
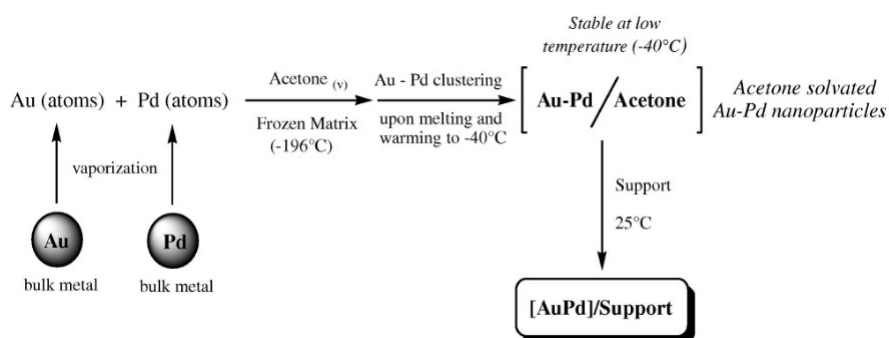
Figure S1: Schematic description of the MVS procedure for preparing PdAu NPs.
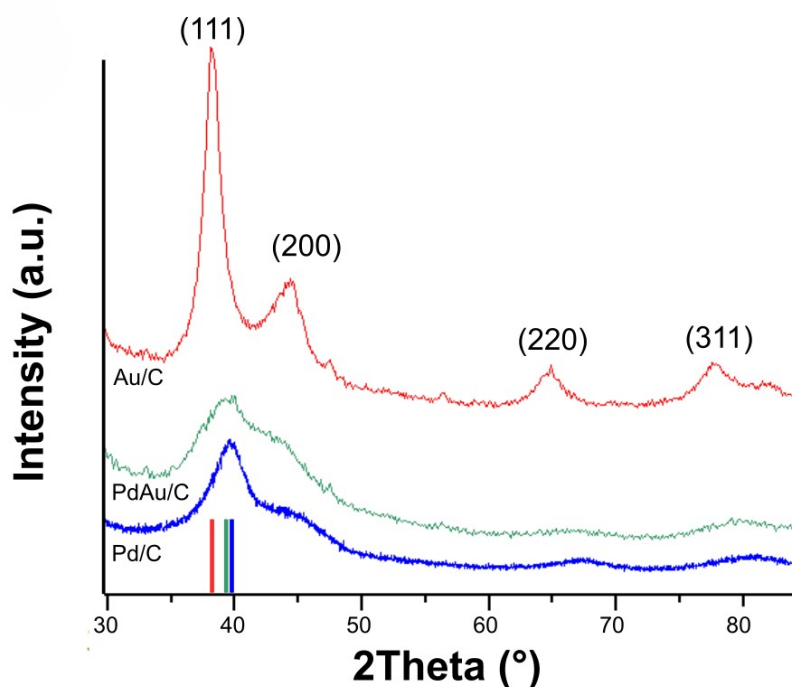

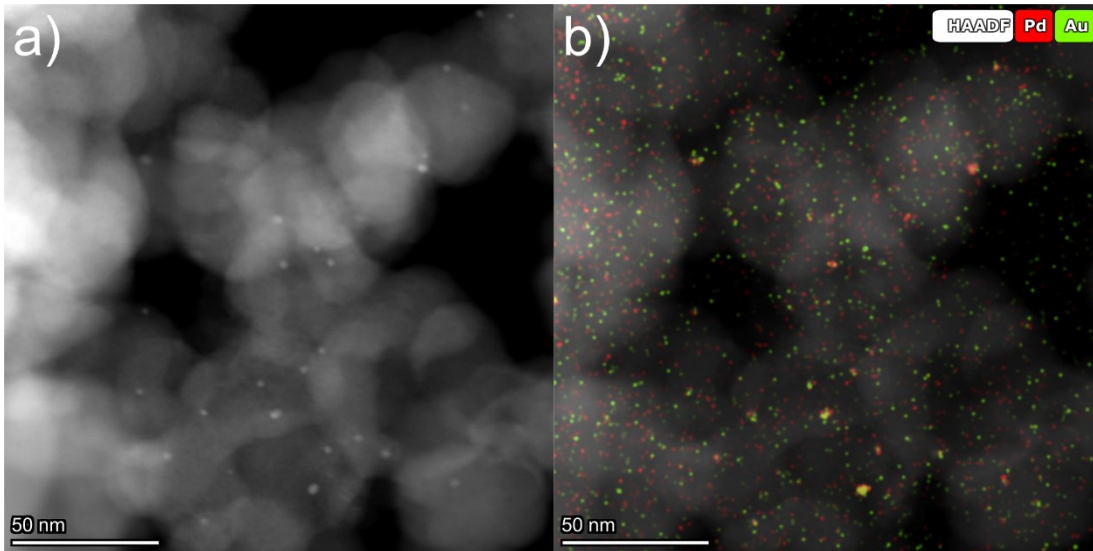Figure S2: (a) Powder XRD pattern comparison of PdAu/C, Au/C and Pd/C.

Figure S3: HAADF image of Au-Pd/C and EDX analysis.

Energy Calculations

The delivered energy for a single fuel load was evaluated by applying Eq. 1, integrating the galvanostatic curve (V vs. time) over the time up till when a negligible cell potential was reached (ca. 0 V).

$$E = I \int_0^t V(t) dt$$

(1)

Where:

I is constant total current flowing through the cell;

$V(t)$ is the transient cell voltage.

To investigate the fuel utilization, the Faradic efficiency is defined as:

$$\eta = \frac{discharge\ capacity}{theoretical\ discharge\ capacity} = \frac{\int_0^t I(t) dt}{2 C_f V_F F}$$

(2)

Where:

$I(t)$ is the transient discharge current;

C_F is the initial formate concentration;

V_F is the formate solution volume;

F is the Faraday constant.

The Faradic efficiency defined in Eq. 2 indicates the ratio of the actual discharging capacity to the theoretical discharging capacity.

ε is defined as the energy efficiency for the complete oxidation of formate to carbonate, according to equation 6:
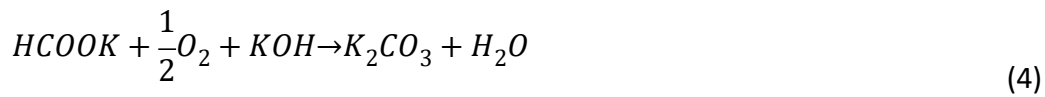
$$\varepsilon = \frac{E}{-M \times \Delta H^0}$$

(3)

Where:

E is the delivered energy from the single cell;

M is the total moles of formate in the cell;

$\Delta H^0_{complete}$ represents the enthalpy for formate oxidation to carbonate reaction (-254.14 KJ mol^{-1}) as shown by equation 7.

$$HCOOK + \frac{1}{2}O_2 + KOH \rightarrow K_2CO_3 + H_2O$$

(4)

It is worthwhile mentioning that Eq. 6 is a comprehensive description of the efficiency efficiency, which accounts for the contribution of thermodynamics, kinetics (activation overpotential and ohmic drop) and ability to convert completely the fuel load (which accounts for the faradic conversion, and any form of fuel loss that may occur in the cell which is always less than 1).
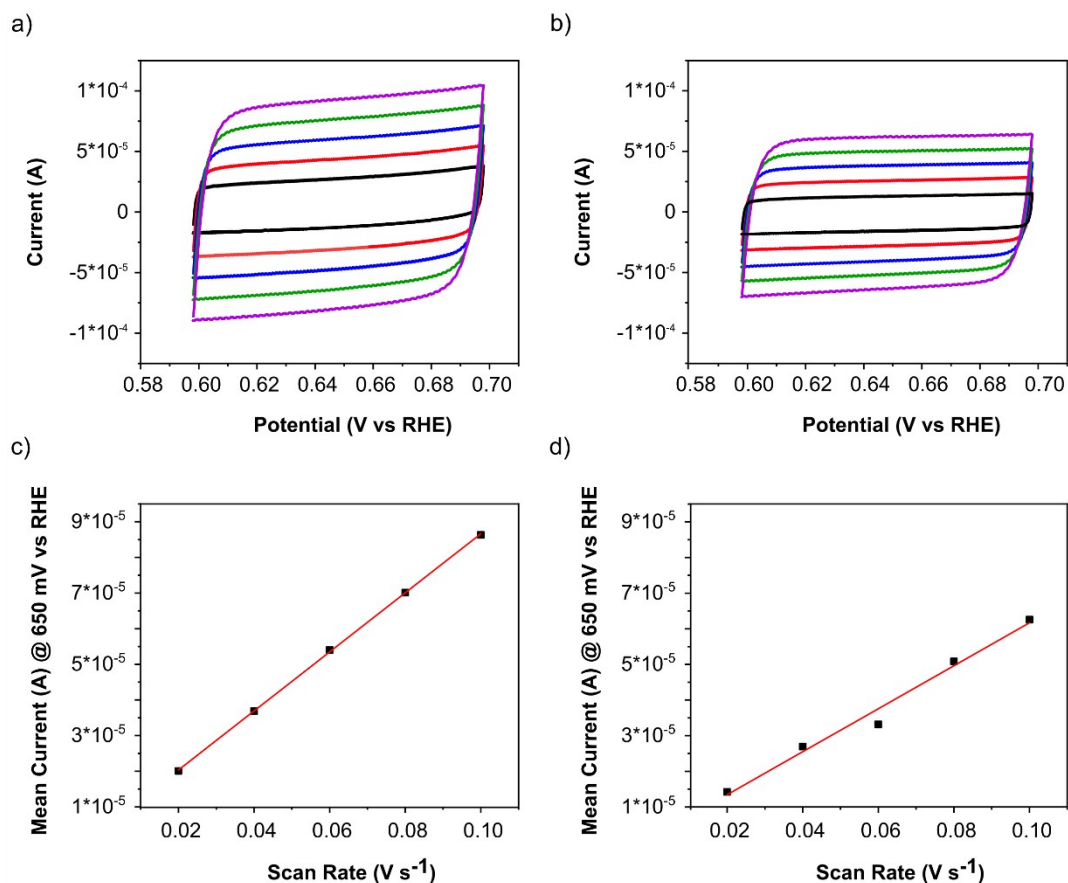
Figure S4. CVs of a) PdAu/C, and b) Pd/C at scan rates of 20, 40, 60, 80, 100 mV s^{-1} in 0.1 M KOH. Corresponding capacitive current at 0.65 V vs scan rate plots for (c) PdAu/C and (d) Pd/C.

Table S1: BET surface area data.

	Metal loading %	BET m^2 g^{-1}	Tot. pore volume cm^3 g^{-1}	Mean pore size nm
PdAu/C	9$_{Pd}$3$_{Au}$	85	0.81	33
Pd/C	10$_{Pd}$	137	0.81	25

Table S2: Important fuel cell data (average of five consecutive cycles with the same MEA with new fuel solutions). Energy calculations described in the Supporting Information.

	OCV mV	R mΩ	Max power density mW cm^{-2}	Max current density mA cm^{-2}	Energy J	η %	ε %	Conversion %
PdAu/C	955	74	137	574	8382	80	33	80
Pd/C	905	49	115	706	6384	65	25	65

Table S3: Comparison of DFFC performance data from recent literature reports.

Anode Catalyst Catalyst laoding mg cm-2	Pd loading mg cm-2	Cathode catalyst	Membrane	Fuel PF:KOH mol L-1	Temp °C	PP mW cm-2	EE %	FE %	Ref
PdAu/C 0.8	0.8	FeCo/C	Fumatech	1:1	60	140	33	80	This work
Pd/C 1.3	1.3	FeCo/C	Fumatech	1:1	60	115	25	65	This work
Pd-CeO$_2$/C 2	2	FeCo/C	A201	4:4	60	243	46	89	1
Pd/C 2	2	FeCo/C	A201	4:4	60	258	42	88	2
PdAu/C	3	Pt/C	Nafion 117	1:2	60	12.3	nd	nd	3
Pd/C	2	Pt/C	A201	1:1	60	125	nd	nd	4
Pd/C	2	FeCo-HYPERMEC	QAPSF	1:1	60	110	nd	nd	3

References:

1. H. A. Miller, J. Ruggeri, A. Marchionni, M. Bellini, M. V. Pagliaro, C. Bartoli, A. Pucci, E. Passaglia and F. Vizza, *Energies*, 2018, **11**.
2. L. Q. Wang, M. Bellini, J. Filippi, M. Folliero, A. Lavacchi, M. Innocenti, A. Marchionni, H. A. Miller and F. Vizza, *Appl Energ*, 2016, **175**, 479-487.
3. L. Zeng, Z. K. Tang and T. S. Zhao, *Appl Energ*, 2014, **115**, 405-410.
4. A. M. Bartrom and J. L. Haan, *J Power Sources*, 2012, **214**, 68-74.