

Supplementary Materials: Improving the Energy Efficiency of Direct Formate Fuel Cells with a Pd/C-CeO₂ Anode Catalyst and Anion Exchange Ionomer in the Catalyst Layer

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S1: Description of energy calculations.

The delivered energy, faradic efficiency and energy efficiency have been obtained from the galvanostatic data obtained for each single fuel batch. The delivered energy for a single fuel load was evaluated by applying Equation (1), integrating the galvanostatic curve (V versus time) over time until a negligible cell potential was reached (ca. 0 V).

$$E = I \int_0^t V(t) dt \quad (1)$$

where: I is constant current flowing through the cell (250) mA; $V(t)$ is transient cell voltage.

To investigate the fuel utilization, we define the Faradic efficiency as:

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

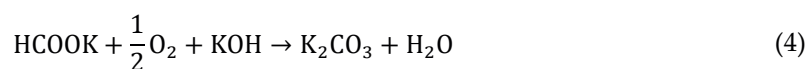
where: $I(t)$ is the transient discharge current; C_F is the initial formate concentration; V_F is the formate solution volume; F is the Faraday constant.

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

The Energy efficiency was determined using Equation (3):

$$\varepsilon = \frac{E}{-M \times \Delta H^0} \quad (3)$$

where E is the delivered energy from the single cell; M is the total moles of formate in the cell; ΔH^0 represents the enthalpy change of formate to carbonate oxidation reaction ($-254.14 \text{ kJ mol}^{-1}$) as shown in Equation (4).



It is worthwhile mentioning that such an energy efficiency definition is comprehensive as it accounts for the thermodynamic efficiency, the potential drop of the cell and the faradaic efficiency which is usually lower than 1 as the conversion is usually not complete.

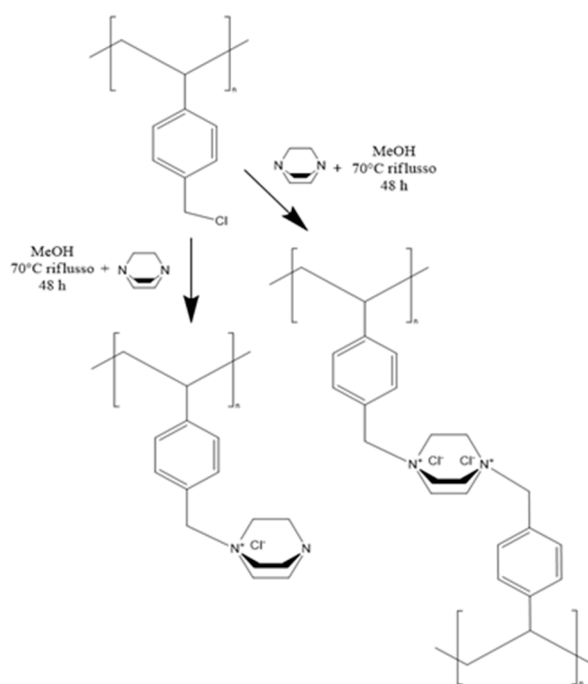


Figure S1: pVBC-DABCO polymeric structure

The ^1H -NMR spectrum of pVBC (Figure S2) confirms the structure of the homopolymer with the expected ratio of integrated aromatic H to CH_2Cl H of 2:1. The molecular weight was determined using gel permeation chromatography (GPC) and confirmed the molar mass and polydispersity typical of pVBC obtained via radical polymerization (Table S1).

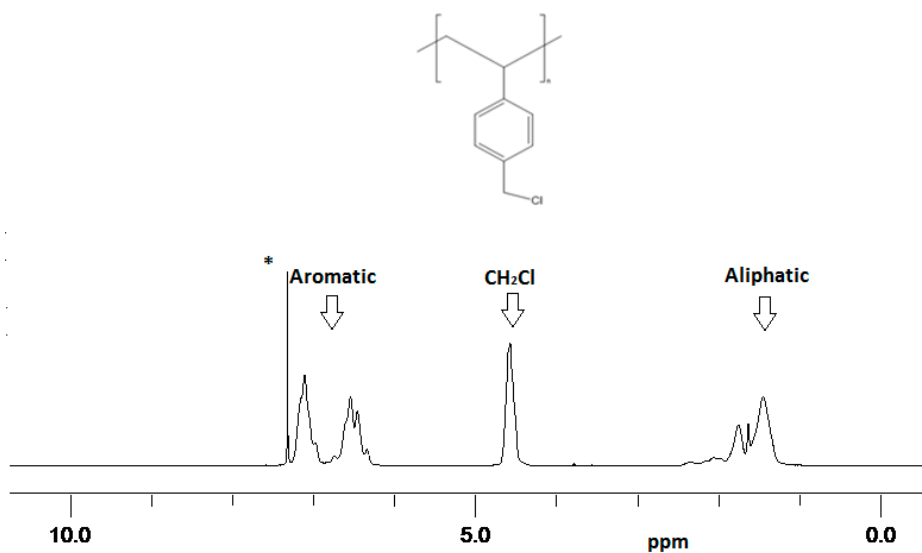


Figure S2: ^1H -NMR spectrum of pVBC.

Table S1: Polymer properties

Polymer	M_w	M_n	M_w/M_n	T_{deg} °C	T_{deg} °C	T_g °C
pVBC	216500	106000	2.04	318	410	112
pVBC-DABCO	-	-	-	241	350	-

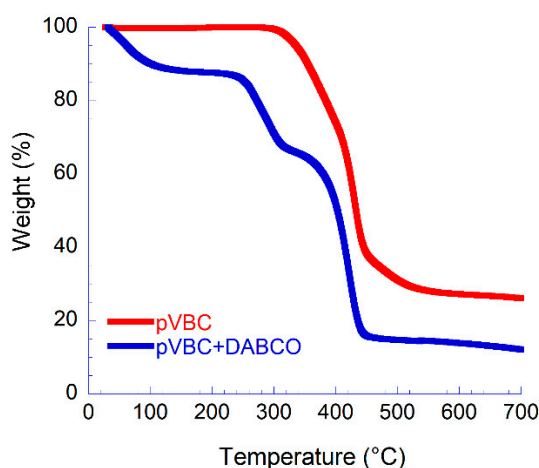


Figure S3: TGA analysis

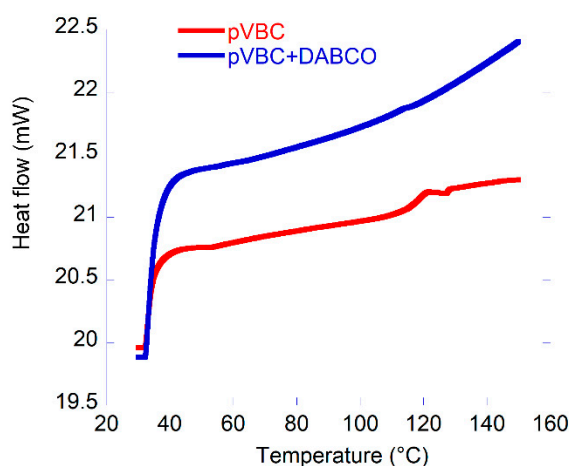


Figure S4: DSC analysis

TGA analysis under nitrogen was carried out on pVBC before and after amination with DABCO (Figure S3). For the pVBC polymer there are two main degradation steps; the first starting at 318 °C due to loss of CH_2Cl groups and after 410 °C due to the destruction of the polymer backbone. After amination, the pVBC-DABCO polymer also undergoes separated degradation steps [1]. Firstly, below 100 °C there is loss of water from the polymer. From 190 to 280 °C due to the loss of the ammonium groups and after 350 °C due to the destruction of the polymer backbone [1]. The decomposition processes for the quaternary ammonium-containing polymer occur at lower temperature, but the material is certainly stable at the temperatures used in the fuel cell (60 °C).

DSC analysis of pVBC and pVBC-DABCO is shown in Figure S4. The DSC curve for pVBC shows a T_g transition round 113 °C. This second-order transition is absent from the DSC curve after reaction with DABCO in the range of temperature investigated (<180 °C) [2,3].

References:

- 1 Vengatesan, S.; Santhi, S.; Sozhan, G.; Ravichandran, S.; Davidson, D. J.; Vasudevan, S. Novel cross-linked anion exchange membrane based on hexaminium functionalized poly(vinylbenzyl chloride). *RSC Adv.* **2015**, *5*, 27365–27371.
- 2 Tsutsui, T.; Tanaka, T. Role of electrostatic forces in the glass transition temperatures of ionic polymers. *Polymer* **1977**, *18*, 817–821.

- 3 Jeevanantham, S.; Hosimin, S.; Vengatesan, S.; Sozhan, G. Quaternized poly(styrene-co-vinylbenzyl chloride) anion exchange membranes: role of different ammonium cations on structural, morphological, thermal and physio-chemical properties. *New J. Chem.* **2018**, 42, 380–387.