Towards an efficient Liquid Organic Hydrogen Carrier fuel cell concept

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Supporting Information

Semi-continuous transfer hydrogenation of acetone with H18-DBT

The semi-continuous transfer hydrogenation experiments were carried out in a 650 mL stainless steel tubular reactor at ambient pressure. The reactor was heated to the desired temperature with an external heating jacket. The reaction temperature in the catalyst bed was measured by two thermocouples (Type K) placed at the bottom and middle of the reactor, respectively. The reactor was equipped with a metal frit at the bottom to hold the catalyst bed (201 g Pt on alumina spheres, 0.3 wt. % Pt, Clariant; catalyst amount corresponded to 0.25 mol% Pt with respect to LOHC-bound hydrogen) and to facilitate acetone evaporation. The reactor was also filled with 393 ml perhydro dibenzyltoluene (H18-DBT) with the liquid being in contact with the entire catalyst material. Prior to each experiment, the reactor setup was purged with argon to ensure inert conditions. Then the reactor was heated to 170 °C. Thereafter, liquid acetone was fed into the reactor with a flow rate of 0,2 mL/min by a HPLC pump (TecLab Minipump) resulting in an acetone gas flow of 100 ml/min and a hydrodynamic residence time of the gaseous reactants of 3.93 min. The start of the HPLC pump marked the beginning of the run. The gaseous reactants left the reactor at the top of the reactor after passing through the catalyst bed in a bubble column manner. This stream of gaseous reactants was condensed by a reflux cooler at 0°C and the resulting liquid was collected in a glass flask. Liquid samples were taken by a three-way walve and were analyzed by gas chromatography (Varian 3900 equipped with a CP Sil PONA CB50 m x 0.21 mm, 0.5 µm capillary column). The non-condensing gaseous reactants were passed through a mass flow meter (MFM, Bronkhorst) after the condenser.

Under these conditions, a yield of 13.6% 2-propanol was detected under the quasi stationary conditions established after one hour reaction time. As main side products, aldol condensation products, e.g. methylisobutylketone, were detected.

Thermodynamics of the oxidation of 2-propanol to acetone

Table S1: Thermodynamic data for molecules involved in the oxidation of 2-propanol to acetone.

	$\Delta G_f^{\ominus}$ (*kJ* mol^{-1})	$\Delta H_f^{\ominus}$ (*kJ* mol^{-1})	$S^{\ominus}$ (J K^{-1} mol^{-1})
2-propanol (liquid)	-180.4	-318.1	+181.1
Acetone (liquid)	-155.4	-248.4	+199.8
Water (liquid)	-237.1	-285.8	+70.0
Oxygen (gas)	0	0	+205.2

Half-reactions

1. CH$_3$COCH$_3$ + 2H$^+$ + 2e$^-$ ⇄ CH$_3$CHOHCH$_3$

$$\Delta G^{\circ}_{\textbf{CH}_3\textbf{COCH}_3/\textbf{CH}_3\textbf{CHOHCH}_3} = \Delta G^{\circ}_{f,\ CH_3CHOHCH_3} - \Delta G^{\circ}_{f,\ CH_3COCH_3} =$$
$$= -180.4\ kJ\ \text{mol}^{-1} - (-155.4\ kJ\ \text{mol}^{-1}) = \textbf{-25.0 }\textit{\textbf{kJ}}\textbf{ mol}^{-1}$$
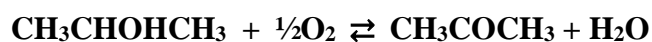
$$\textbf{E}^{\circ}_{\textbf{CH}_3\textbf{COCH}_3/\textbf{CH}_3\textbf{CHOHCH}_3} = -\frac{\Delta G^{\circ}}{zF} = -\frac{-25.0\ kJ\ \text{mol}^{-1}}{2\cdot 96,485\ \text{A s mol}^{-1}} = \textbf{+0.130 V vs SHE}$$

2. O$_2$ + 4H$^+$ + 4e$^-$ ⇄ 2H$_2$O
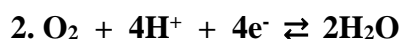
$$\Delta G^{\circ}_{\textbf{O}_2/\textbf{H}_2\textbf{O}} = 2\cdot\Delta G^{\circ}_{f,\ H_2O} = 2\cdot(-237.1\ kJ\ \text{mol}^{-1}) = \textbf{-474.2 }\textit{\textbf{kJ}}\textbf{ mol}^{-1}$$

$$\textbf{E}^{\circ}_{\textbf{O}_2/\textbf{H}_2\textbf{O}} = -\frac{\Delta G^{\circ}}{zF} = -\frac{-474.2\ kJ\ \text{mol}^{-1}}{4\cdot 96,485\ \text{A s mol}^{-1}} = \textbf{+1.229 V vs SHE}$$

Total reaction:

CH$_3$CHOHCH$_3$ + ½O$_2$ ⇄ CH$_3$COCH$_3$ + H$_2$O

$$\Delta G^{\circ}_{\textbf{rxn}} = (\Delta G^{\circ}_{f,\ CH_3COCH_3} + \Delta G^{\circ}_{f,\ H_2O}) - (\Delta G^{\circ}_{f,\ CH_3CHOHCH_3}) =$$
$$(-155.4-237.1\ kJ\ \text{mol}^{-1}) - (-180.4\ kJ\ \text{mol}^{-1}) = \underline{\textbf{-212.1 }\textit{\textbf{kJ}}\textbf{ mol}^{-1}}$$

$$\Delta H^{\circ}_{\textbf{rxn}} = (\Delta H^{\circ}_{f,\ CH_3COCH_3} + \Delta H^{\circ}_{f,\ H_2O}) - (\Delta H^{\circ}_{f,\ CH_3CHOHCH_3}) =$$
$$(-248.4-285.8\ kJ\ \text{mol}^{-1}) - (-318.1\ kJ\ \text{mol}^{-1}) = \underline{\textbf{-216.1 }\textit{\textbf{kJ}}\textbf{ mol}^{-1}}$$

$$\Delta S^{\circ}_{\textbf{rxn}} = (S^{\circ}_{CH_3COCH_3} + S^{\circ}_{H_2O}) - (S^{\circ}_{CH_3CHOHCH_3} + \frac{1}{2}S^{\circ}_{O_2}) =$$
$$(+199.8+70.0\ \text{J K}^{-1}\ \text{mol}^{-1}) - (+181.1+0.5\cdot 205.2\ \text{J K}^{-1}\ \text{mol}^{-1}) = \underline{\textbf{-13.9 J K}^{-1}\textbf{ mol}^{-1}}$$

Thus, the energy efficiency is:

$$\eta = \frac{\Delta G}{\Delta H} = \frac{-212.1 \; kJ \; mol^{-1}}{-216.1 \; kJ \; mol^{-1}} \cong 0.98$$

or

$$\eta = 1 - T\frac{\Delta S}{\Delta H} = 1 - 298.15 \; K \; \cdot \; \frac{-13.9 \; J \; K^{-1} \; mol^{-1}}{-216.1 \; kJ \; mol^{-1}} \cong 0.98$$

Reaction enthalpy for the hydrogenation of acetone:

$$\Delta H_{hyd}^{\circ} = (\Delta H_{f, \; CH_3CHOHCH_3}^{\circ}) - (\Delta H_{f, \; CH_3COCH_3}^{\circ} + \Delta H_{f, \; H_2}^{\circ}) =$$
$$(-318.1 \; kJ \; mol^{-1}) - (-248.4 \; kJ \; mol^{-1} + 0 \; kJ \; mol^{-1}) = \underline{\mathbf{-69.7 \; kJ \; mol^{-1}}}$$
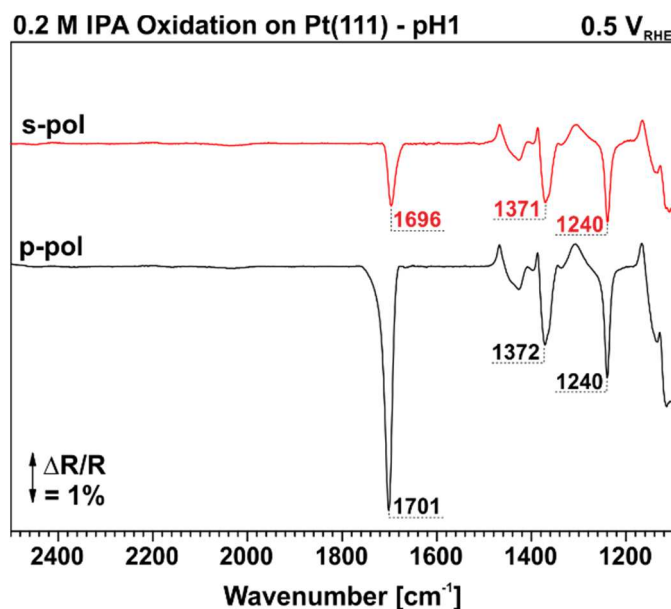
EC-IRRAS spectrum

Figure S1: EC-IRRAS spectra of the 2-propanol oxidation (0.2 M 2-propanol) on Pt(111) in 0.1 M HClO$_4$ measured at 0.5 V$_{RHE}$ in s- and p-polarisation The reference spectra were acquired at 0.05 V$_{RHE}$.

Linear sweep voltammogram on PtRu/C

From a slow linear potential sweep (1 mV s^{-1}) in a 0.1 M HClO$_4$ + 0.2 M 2-propanol solution, we found that the rate of the reaction on PtRu/C shows a maximum at ca. +0.18 V vs the RHE (Figure S2). As the measurement was performed in a flow cell, the appearance of a rate maximum is not related to limitations in the mass transport of 2-propanol. A more reasonable explanation is that oxidation of ruthenium surface atoms occurs at this potential and is detrimental for catalytic activity. The shape of the voltammogram in Figure S2 explains the maximum in current density observed in the j-U-curve at 0.55 V in Figure 2a.
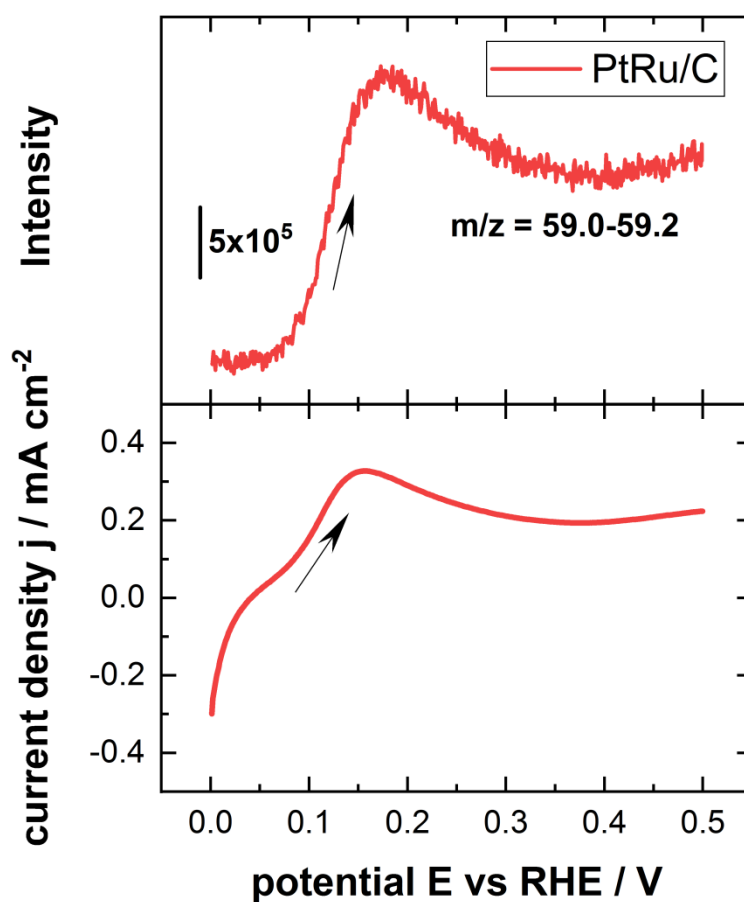

Figure S2: Positive-going linear sweep voltammogram (bottom panel) and acetone production rate determined with EC-RTMS (top panel) on PtRu/C in 0.1 M HClO$_4$ + 2-propanol. Sweep rate: 1 mV s^{-1}.

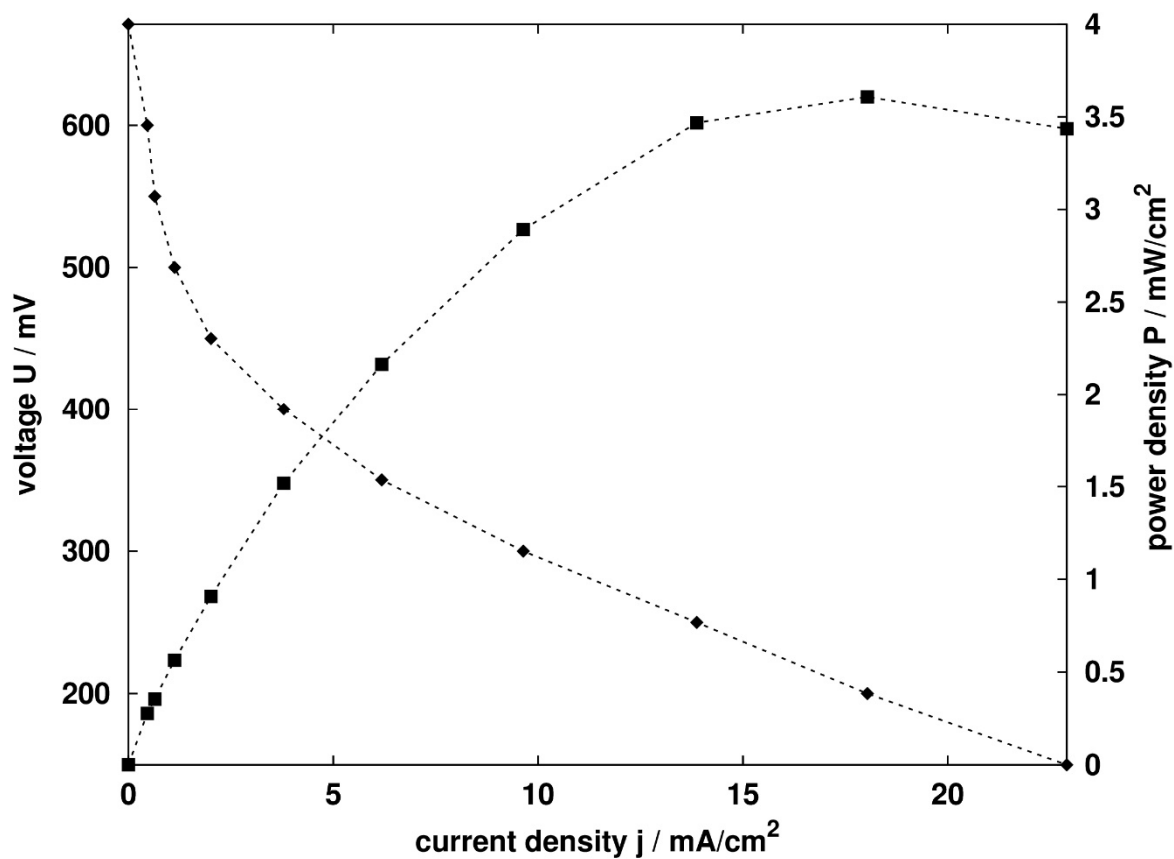**2-propanol FC using a MEA with pure Pt as the anode catalyst**

Figure S3: Current density-voltage and current density-power density-curves of 2-propanol on a MEA using Pt as anode catalyst. Conditions: T = 85 °C, 50 g h^{-1} 2-propanol, 1 L$_N$ min^{-1} nitrogen, 1 L$_N$ min^{-1} pressurized air. Material: CCM with a Nafion® 115 membrane and 0.3 mg cm-1 Pt loading on each side combined with Sigracet® 10BC as GDL.