Journal of Materials Chemistry A

Supplementary information

Mechanism of ion conductivity through polymer stabilized CsH_2PO_4 nanoparticular layers from experiment and theory

S1: Details of the spray drying process

Set of spray dryer and precursor parameters used to deposit nanostructured solid acid fuel cell electrodes.

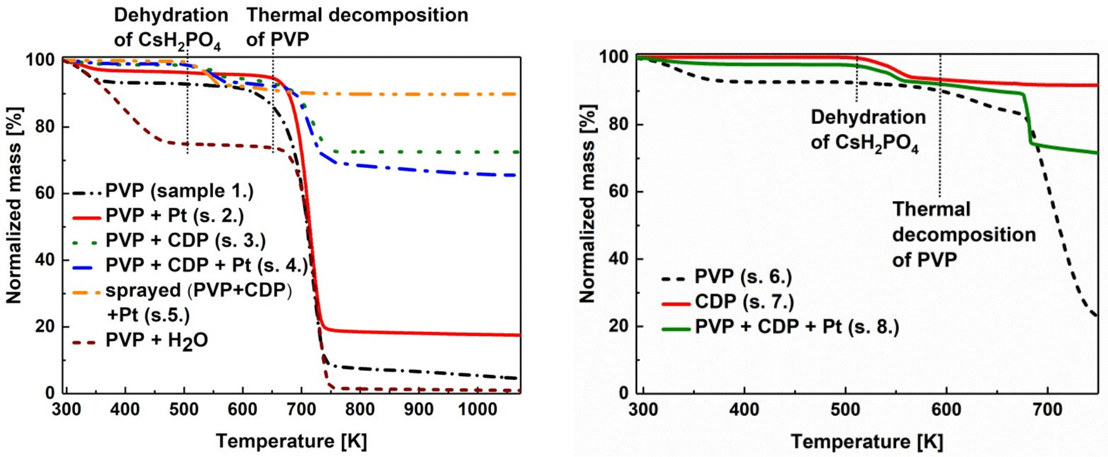
Precursor parameters			Spray dryer parameters			
CsH_2PO_4 conc.	Methanol content	PVP conc.	Temp.	Carrier gas flow rate	Precursor solution flow rate	Atomizer mesh size
10 g l^{-1}	44 wt%	0.3 g l^{-1}	303 K	80 l min^{-1}	1.5 ml min^{-1}	4 µm

S2: Details of the thermogravimetric analysis (TGA)

Compositions of samples for thermogravimetric analysis.

Sample	Atmosphere	PVP wt%	CsH_2PO_4 wt%	Pt wt%
1	Nitrogen	100	0	0
2	Nitrogen	80	0	20
3	Nitrogen	27	73	0
4	Nitrogen	24	66	10
5*	Nitrogen	3	87	10
6	Air	100	0	0
7	Air	0	100	0
8	Air	25	70	5

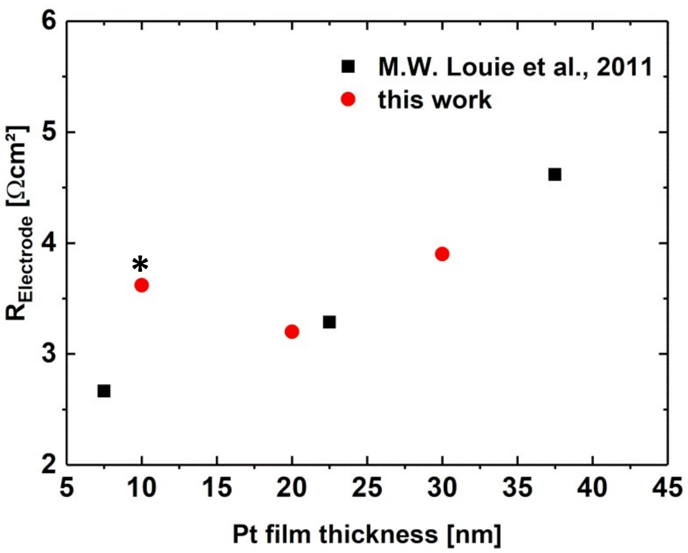
*CsH_2PO_4 and PVP deposited by spray drying.



Thermogravimetric analysis (Heat rate 10 K min^{-1}) of polyvinylpyrrolidone (1,300,000 g mol^{-1}) and mixtures of CsH_2PO_4 and/or Pt black nanoparticles, obtained by mixing powders or spray drying. Left: nitrogen atmosphere. Right: Air. Dashed lines show the dehydration of CsH_2PO_4 and thermal decomposition of PVP.

We observe a slight initial dip in the TGA curves around 370 K due to desorption and evaporation of water. A second dip in the TGA curves is observed for all CsH_2PO_4-containing samples due to the dehydration of the solid acid compound slightly above 500 K. This is equal in both gas atmospheres. In a nitrogen atmosphere the thermal decomposition of PVP occurs slightly above 650 K. Within an air atmosphere, a small mass loss can be detected for pure PVP above 600 K. In sample 8, the onset of this mass loss is hard to determine. Both PVP containing samples (sample 6 and 8) show a fast mass loss above 670 K. In summary stability at the operating temperature (513 K) of pure PVP, as well as mixtures with CsH_2PO_4 and Pt are confirmed in both air and nitrogen.

S3: Comparison of thin film electrodes with literature



Comparison of electrode resistance values for thin film Pt electrodes deposited on polished CsH_2PO_4 disks with data obtained by M. W. Louie and S. M. Haile. The electrode marked with an asterisk was not stable. [M. W. Louie, S. M. Haile, Energy & Environmental Science 2011, 4, 4230.]

To verify the used setup and guarantee comparability to the data published by other groups, Pt thin film electrodes were fabricated. Thin film Pt electrodes (20 and 30 nm thickness) on polished electrolyte disks were in good agreement with data published by Louie et al. The electrode impedance for 10 nm Pt thin film did not reach stability due to continued coarsening of the catalyst film. Thicknesses of 10 nm are out of the optimal working range of the used sputtering machine. Louie et al. observed the same problem for films below 7 nm.

S4: Supplementary information for the analytical model

Model parameters	Abbreviation	Value
Resistivity of CsH_2PO_4	ρ	45.45 Ω cm
Electrode length	l	20.0 µm
Electrode area	A	1.0 cm²
Number of columns	N_{Col}	
Column area		$7.85*10^{-9}$ cm²
Column length		20.0 µm
Length of one constriction	l_{const}	300.0 nm
Area of one constriction	A_{const}	$7.07*10^{-10}$ cm²

In general, the resistance of a conductor is calculated as followed:

$$R = \rho \frac{l}{A}$$

With: “*R*”: resistance, “*l*”: length, “*A*”: area and “*ρ*”: resistivity of the conductor. With R_{area} as area normalized resistance, the equation can be written as:

$$R_{area} = \rho * l$$

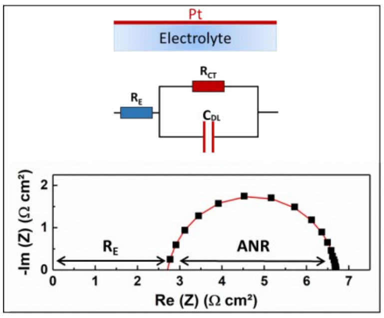
In the analytical model, the porosity is simulated by free standing columns with a diameter of 1 µm and a space filling of 50%. For a cell area of 1 cm², this results in N_{Col}=6.37*10^{7} with the resistance of each column R_{Col}= 1.16*10^{7} Ω. Since all columns can be regarded equal resistors in a parallel circuit, R_{area} is calculated as followed:

$$\frac{1}{R_{area}} = \sum_{i=1}^{n} \frac{1}{R_i} \rightarrow \frac{1}{R_{area}} = N_{col} \frac{1}{R_{col}} \rightarrow R_{area} = \frac{R_{Col}}{N_{Col}}$$

Constructions are simulated as columns of a diameter of 150 nm and a length of 300 nm in series to the 1 µm diameter columns.

S5: electrode impedance

Processes measured with impedance spectroscopy can be analysed using an equivalent circuit. As an approximation, an electrode can be described by a parallel R-C circuit with the charge transfer resistance (R_{CT}) and the double layer capacitance (C_{DL}) representing the hydrogen oxidation reaction and an ohmic resistance R_E in series for the electrolyte resistance.

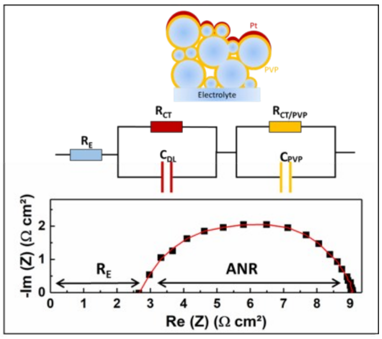


Equivalent circuit model for a platinum thin film electrode with the charge transfer resistance (R_{CT}), the double layer capacitance (C_{DL}) and electrolyte resistance R_E.

When applying a porous layer on a dense CsH_2PO_4 pellet, the surface area increases as well as the active side density after platinum is sputtered on top. This decreases the charge transfer resistance resulting in a smaller impedance arc. Since sputtering is a line of site deposition technique, platinum will only reach the top 5 µm of the porous structure as stated by Suryaprakash et al. (RSC Adv. 2014, 4, 60429 – 60436). A further increase of the porous structure does not further increase the active site density and should therefore only affect the electrolyte resistance R_E. Since the Impedance (Z) is calculated by:

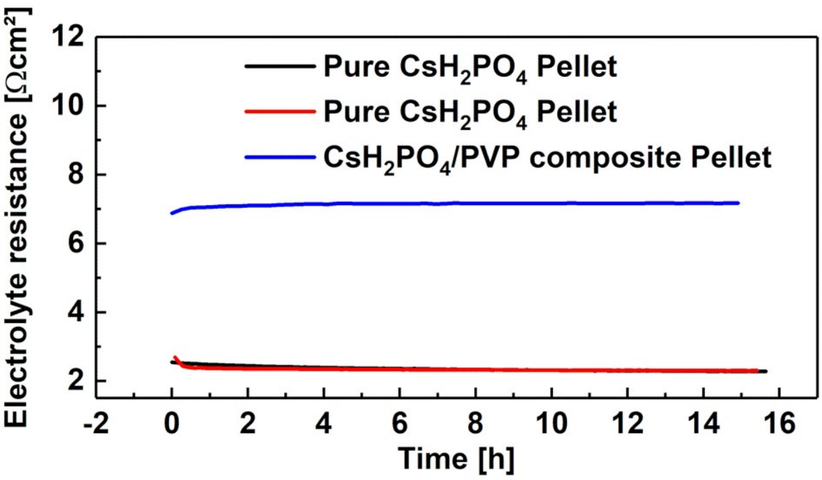
$$Z(f) = R_E + \frac{R_{CT}}{1 + i2\pi R_{CT} C_{DL}}$$

Purely ohmic resistances don't have an impact on the ANR. As stated in the paper, at the boundary between CsH_2PO_4 and PVP, a chemical double layer can develop, transforming the porous electrolyte into a frequency dependent resistance. Consequently the equivalent circuit model has to be adapted by adding an additional R/C circuit in series which affects the arc width (ANR) as well as the arc symmetry.



Equivalent circuit model for a porous PVP containing electrode with the charge transfer resistance (R_{CT}), the double layer capacitance (C_{DL}), electrolyte resistance R_E, the PVP related resistance $R_{CT/PVP}$ and the PVP related double layer capacitance C_{PVP}.

S6: Influence of PVP on conductivity



Area-normalized electrolyte resistance obtained from symmetrical cells. Cells were either 500 µm-thick pure CsH_2PO_4 pellets or a composite pellet containing a 500 µm pure CsH_2PO_4 pellet with a 100 µm-thick dense layer of spray dried CsH_2PO_4 + PVP mixture. The additional PVP-containing layer increases the electrolyte resistance from 0.8 Ω cm^2 to ca. 2.2 Ω cm^2. This represents an 11-fold decrease in conductivity for the sprayed layer.