Determining HTPEM electrode parameters using a mechanistic impedance model

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Introduction

The purpose of this work is to enable extraction of unknown MEA parameters from EIS and polarisation curve data. This is attempted by fitting a model to polarisation curve and impedance data simultaneously. The aim is to reduce the risk of obtaining a good fit with non-realistic parameters.

Model

The fuel cell model is implemented using a 2D finite volume approach, taking into account variations across the membrane and along the channel. The model solves a system of 1542 nonlinear equations. The model can be solved in steady state to generate polarisation curves and in dynamic mode to generate impedance spectra. The model is written using Matlab®. Table 1 lists the equations taken into account by the model and the subdomains in which they are solved.

Experimental

The MEA was prepared and tested at the School of Chemical Engineering and Advanced Materials, Newcastle University. The membrane was PBI doped with 5.6 H_3PO_4 PRU. The catalyst layers were made with Pt/C catalyst mixed with PTFE and doped with H_3PO_4. The anode used 20% Pt/C catalyst and a loading of 0.2 mg Pt/cm^2. The cathode used 40% Pt/C catalyst with a loading of 0.4 mg Pt/cm^2. The cell active area was 9 cm^2. Reactant flow rates were 0.45 L/min for air and 0.2 L/min fro H_2. Cell temperature was 150^{o}C

Results

The model is fitted to a data set consisting of one polarisation curve and three impedance spectra. Plots of the fitted curves and the data can be seen on the right. Tables 2 and 3 give the fitted parameter values and the achieved fit quality.

Discussion

The fit to the polarisation curve is quite good in most of the points. At low current density performance is overestimated. This is presumably because the model does not account for H_2 cross-over. At high current density the mass transport losses seem overestimated. This suggests that the acid film thickness is too large.

The impedance spectra fits have a number of problems. While the polarisation curve fit is good around 0.32 A/cm^2, the impedance fit is quite poor at this point. This indicates that there are important phenomena influencing the impedance that the model does not account for. One possible explanation could be that the assumption of single step electrode kinetics is not sufficient to account for the dynamic response of the fuel cell. Introducing a multi step reaction mechanism might increase the impedance in the low frequency region, where the fit is poorest.

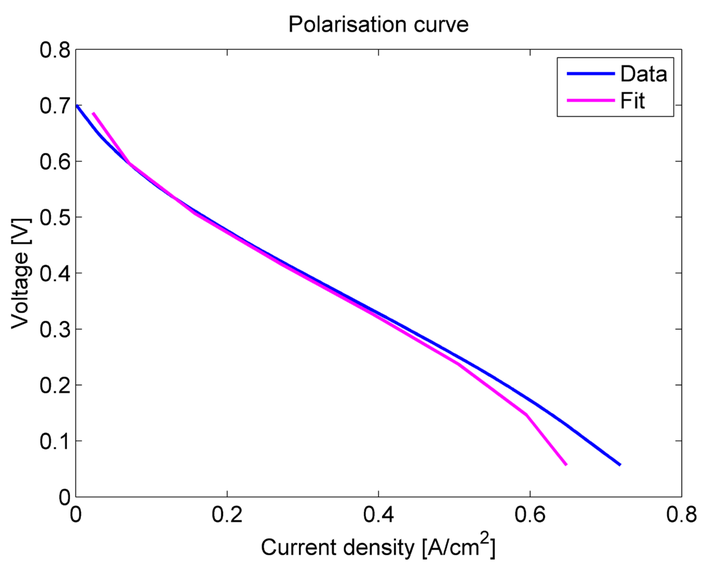
At high frequency the shapes of the simulated spectra deviate significantly from the data. Since the shape at high frequency is influence by the CL conductivity, the fitted value of the CL conductivity may be too high.

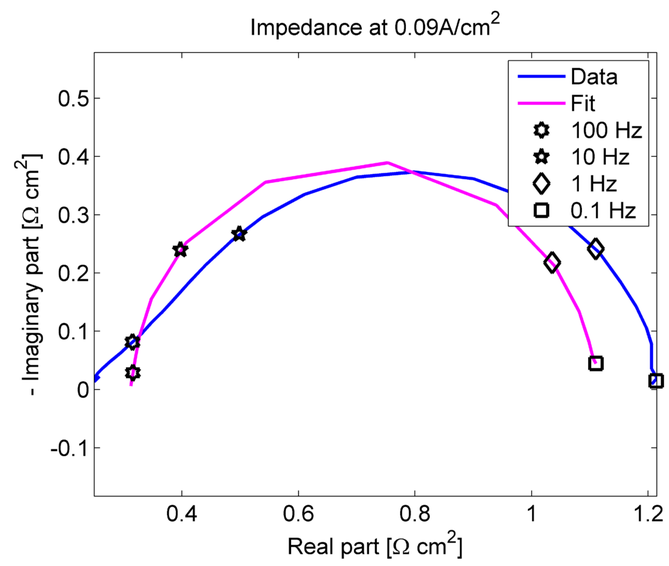
In all cases the high frequency intercept occurs at a higher value of the impedance real part in the simulation than in the data. This indicates that the ohmic losses are exaggerated. This is more pronounced at higher current density.

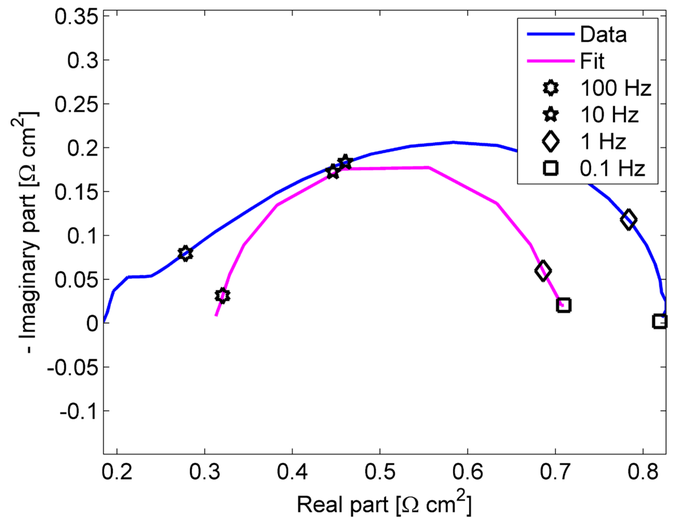
The model assumes constant CL and membrane conductivity. Calculating the conductivity as a function of water content may improve the correlation at high current density. This may also give a more realistic value of the catalyst layer conductivity.

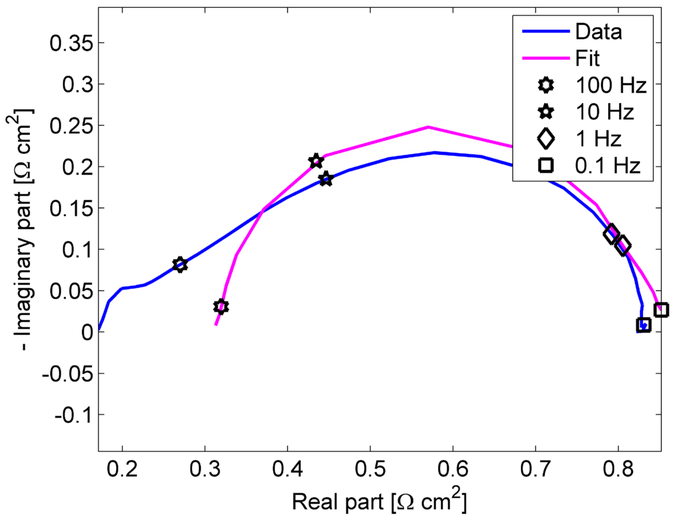
Equations solved	Model subdomains								
	Anode				Membrane	Cathode			
	Channel	GDL	MPL	CL		CL	MPL	GDL	Channel
Continuity	x	x	x	x		x	x	x	x
Momentum	x	x	x	x		x	x	x	x
O2 transport						x	x	x	x
H2O transport	x	x	x	x	x	x	x	x	x
Reaction kinetics				x		x			
Reactant diffusion in electrolyte film				x		x			
Ionic potential				x	x	x			

Table 1: Model equations and subdomains









Fitted parameters					
Anode catalyst area	49.6 m^2/m^2	Membrane Conductivity	1.31 S/m	GDL porosity	0.847
Cathode catalyst area	223 m^2/m^2	CL conductivity	9.48 S/m	Cathode charge transfer coefficient	0.627
Anode Capacitance	9.80e5 F/m^3	CL porosity	0.353	CL acid film Thickness	887 nm
Cathode Capacitance	4.40e6 F/m^3	MPL porosity	0.677	Membrane water diffusion coefficient	1.81e-10 m/s^2

Table 2: Fitted parameter values

Fit quality (Normalised RMS deviation):	
Total	18.8 %
Polarisation curve	4.12 %
Mean EIS	18.3 %
EIS at 0.09 A/cm^2	12.5 %
EIS at 0.32 A/cm^2	23.9 %
EIS at 0.51 A/cm^2	16.7%

Table 3: Fit quality

Conclusions

- A 2D finite volume based HTPEM fuel cell model capable of simulating impedance spectra and polarisation curves has been developed.
- The model was fitted to one polarisation curve and three impedance spectra simultaneously.
- An acceptable fit to the polarisation curve has been achieved but a good fit to the impedance spectra could not be achieved simultaneously.
- The main reason for the poor fit is assumed to be the assumption of single step reaction kinetics.
- Future work includes the introduction of a multi step electrode model and calculation of conductivity based on electrolyte water content.

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