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# Empirical Aging Model

Loss of electrochemical surface area (ECSA) in polymer electrolyte fuel cell cathodes has been reported in literature. The published data has been fit by the function

$$\frac{ECSA}{ECSA_0} = C - \frac{1}{B}\operatorname{asinh}\left(\sinh\left(B(C-1)\right)N^{A\cdot B}\right)$$

Where $N$ is the number of rectangular wave voltage cycles 1-40,000.

$$A = a(1 + b\cdot RH)(1 + c\ln(1 + t_{UPL}))(1 + d\ln(1 + t_{LPL})) \times \exp\left(-\frac{E_{aA}}{RT}\right)\exp\left(e\frac{F}{RT}(V_{UPL} - V_0)\right)\exp\left(f\frac{F}{RT}(V_{LPL} - V_0)\right)$$

$$B = \alpha(1 + \beta\cdot RH)(1 + \gamma\ln(1 + t_{UPL}))(1 + \delta\ln(1 + t_{LPL})) \times \exp\left(-\frac{E_{aB}}{RT}\right)\exp\left(\varepsilon\frac{F}{RT}(V_{UPL} - V_0)\right)\exp\left(\zeta\frac{F}{RT}(V_{LPL} - V_0)\right)$$

The value of $C = 1.001$ and $V_0 = 0.98\ V$ were selected after hand fitting. $R$ is the ideal gas constant 8.314 J/molK. $F$ is Faraday constant 96485.3 C/mol. Range of test conditions explored experimentally

| Condition | min | max |
|---|---|---|
| $t_{UPL}\ [s]$ | 2 | 300 |
| $t_{LPL}\ [s]$ | 2 | 300 |
| $V_{UPL}\ [V]$ | 0.8 | 1 |
| $V_{LPL}\ [V]$ | 0.4 | 0.8 |
| $T\ [K]$ | 333.15 | 363.15 |
| $RH$ | 0.4 | 1 |

$RH$ is relative humidity, $t_{UPL}$ is time at upper potential limit, $t_{LPL}$ is time at lower potential limit, $V_{UPL}$ is potential of the upper potential limit, $V_{LPL}$ is potential of the lower potential limit, $T$ is temperature. The values of $a$ and $\alpha$ were fit separately for each of 4 data sets as

| Data Set | $a$ | $\alpha$ |
|---|---|---|
| 1 | -22163752.7431349 | -2.25221786507963E-08 |
| 2 | -15408951.2692112 | -4.49901468280169E-08 |
| 3 | 15506864.2681064 | 4.81199254792549E-08 |
| 4 | 16752576.6578532 | 3.20039164223396E-08 |

The values of the other parameters were fit simultaneously to the 4 data sets as

| | |
|---|---|
| b | -0.330745112261277 |
| c | 0.0422225897309428 |
| d | -0.0252559223825606 |
| e | 0.152227535372688 |
| f | -0.200580393019062 |
| $\beta$ | 1.72956278312408 |
| $\gamma$ | 0.0367292597803257 |
| $\delta$ | 0.0366750190665531 |
| $\varepsilon$ | -0.102617650203082 |
| $\zeta$ | 0.213272924462045 |

And

| | |
|---|---|
| $E_{aA}\ [J/mol]$ | 60500.9981580511 |
| $E_{aB}\ [J/mol]$ | -59281.5159646116 |