The ImpedanceAnalyzer:

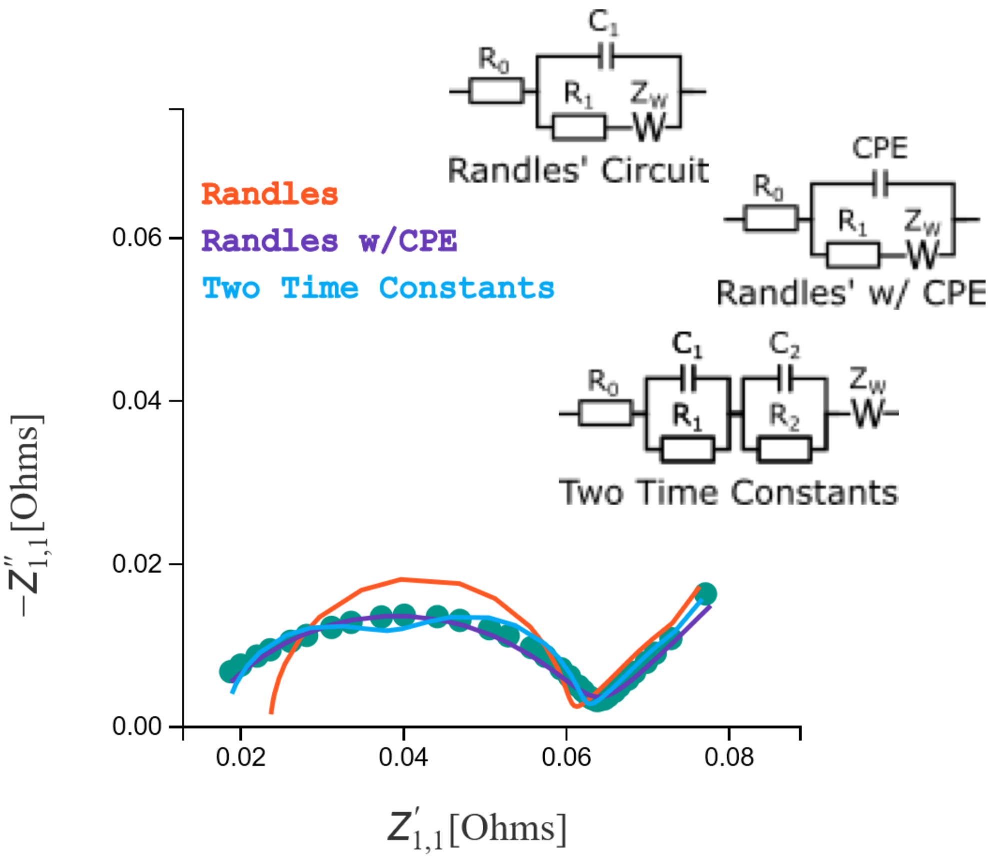
An open-source, web-based tool for sophisticated interrogation of experimental EIS spectra

Matthew D. Murbach, Victor W. Hu, and Daniel T. Schwartz

University of Washington, Seattle
Department of Chemical Engineering
Clean Energy Institute

Tuesday, 3 October 2017
232nd ECS Meeting, National Harbor, MD

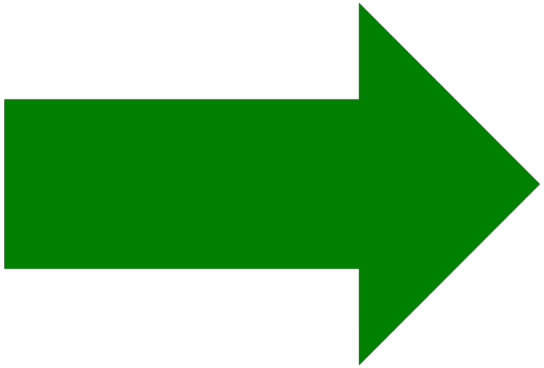
Standard analysis of EIS spectra involves fitting a circuit



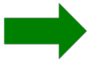
Equivalent circuits can capture **differences** in spectra, but complex circuits can have **tenuous connections to physics**

Fitting physics-based models to EIS data is rare

- 100s of papers using P2D model for battery simulation and design
- 3 of top 10 citations in Journal of Electrochemical Society



- Only a handful of models ever applied to impedance analysis
- Huge loss in translating from modeling to experimental application



M. Doyle, J. P. Meyers, and J. Newman, *J. Electrochem. Soc.*, **147**, 99–110 (2000)
Q. Guo, V. R. Subramanian, J. W. Weidner, and R. E. White, *J. Electrochem. Soc.*, **149**, A307 (2002)
G. Sikha and R. E. White, *Journal of The Electrochemical Society*, **155**, A893 (2008)
D. P. Abraham, S. Kawauchi, and D. W. Dees, *Electrochimica Acta*, **53**, 2121–2129 (2008)

Physics-based models are hard for experimentalists to use

Solid-Phase Material Balance

Real: $\epsilon\omega_1 c^{s''}_{1,1} = \frac{1}{r^2}\frac{\partial}{\partial r}(D_s r^2 \frac{\partial c^{s'}_{1,1}}{\partial r})$ [A1.1r]

Imaginary: $-\epsilon\omega_1 c^{s'}_{1,1} = \frac{1}{r^2}\frac{\partial}{\partial r}(D_s r^2 \frac{\partial c^{s''}_{1,1}}{\partial r})$ [A1.1i]

BC at $r = R_p$: $-D_s \frac{\partial c^{s'}_{1,1}}{\partial r} = j_f{}'_{1,1}$

$-D_s \frac{\partial c^{s''}_{1,1}}{\partial r} = j_f{}''_{1,1}$

BC at $r = 0$: $\frac{\partial c^{s'}_{1,1}}{\partial r} = 0$ $\frac{\partial c^{s''}_{1,1}}{\partial r} = 0$

Solution-Phase Material Balance

Real: $\frac{\partial}{\partial x}(D_{eff} \frac{\partial c'_{1,1}}{\partial x}) =$ [A1.2r]
$\epsilon\omega_1 c''_{1,1} - a(1 - t^0_+)(j_f{}'_{1,1} + j_{dl}{}'_{1,1})$

Imaginary: $\frac{\partial}{\partial x}(D_{eff} \frac{\partial c''_{1,1}}{\partial x}) =$ [A1.2i]
$-\epsilon\omega_1 c'_{1,1} - a(1 - t^0_+)(j_f{}''_{1,1} + j_{dl}{}''_{1,1})$

BC at $x = 0$ and $x = l_{neg} + l_{sep} + l_{pos}$:
$\frac{\partial c'_{1,1}}{\partial x} = 0$ $\frac{\partial c''_{1,1}}{\partial x} = 0$

Faraday's Law

Real: $\frac{\partial i_2{}'_{1,1}}{\partial x} = aF(j_f{}'_{1,1} + j_{dl}{}'_{1,1})$ [A1.3r]

Imaginary: $\frac{\partial i_2{}''_{1,1}}{\partial x} = aF(j_f{}''_{1,1} + j_{dl}{}''_{1,1})$ [A1.3i]

BC at $x = 0$ and $x = L$: $i_2{}'_{1,1} = 0$ $i_2{}''_{1,1} = 0$

BC at $x = l_{neg}$ and $x = l_{neg} + l_{sep}$: $i_2{}'_{1,1} = -1$
$i_2{}''_{1,1} = 0$

Solid-Phase Potential

Real: $-\sigma_{eff} \frac{\partial \varphi^{s\,'}_{1,1}}{\partial x} = -1 - i_2{}'_{1,1}$ [A1.4r]

Imaginary: $-\sigma_{eff} \frac{\partial \varphi^{s\,''}_{1,1}}{\partial x} = -i_2{}''_{1,1}$ [A1.4i]

BC at $x = 0$ and $x = L$: $\sigma_{eff} \frac{\partial \varphi^{s\,'}_{1,1}}{\partial x} = 1$
$\frac{\partial \varphi^{s\,''}_{1,1}}{\partial x} = 0$

BC at $x = l_{neg}$ and $x = l_{neg} + l_{sep}$: $\frac{\partial \varphi^{s\,'}_{1,1}}{\partial x} = 0$
$\frac{\partial \varphi^{s\,''}_{1,1}}{\partial x} = 0$

Solution-Phase Potential

Real: [A1.5r]
$-\kappa_{eff} \frac{\partial \varphi'_{1,1}}{\partial x} = i_2{}'_{1,1} - \frac{2\kappa_{eff} RT}{c_0 F}(1 - t^0_+)\frac{\partial c'_{1,1}}{\partial x}$

Imaginary: [A1.5i]
$-\kappa_{eff} \frac{\partial \varphi''_{1,1}}{\partial x} = i_2{}''_{1,1} - \frac{2\kappa_{eff} RT}{c_0 F}(1 - t^0_+)\frac{\partial c''_{1,1}}{\partial x}$

BC at $x = 0$: $\varphi'_{1,1} = 0$ $\varphi''_{1,1} = 0$

BC at $x = l_{neg} + l_{sep} + l_{pos}$: $\frac{\partial \varphi'_{1,1}}{\partial x} = 0$
$\frac{\partial \varphi''_{1,1}}{\partial x} = 0$

Faradaic Flux

Real: $j_f{}'_{1,1} = \frac{i_0(\alpha_a + \alpha_c)}{RT}\eta'_{1,1}$ [A1.6r]

Imaginary: $j_f{}''_{1,1} = \frac{i_0(\alpha_a + \alpha_c)}{RT}\eta''_{1,1}$ [A1.6i]

Double-layer Flux

Real: $j_{dl}{}'_{1,1} = \omega_1 \frac{C_{dl}}{F}(\varphi^{s\,''}_{1,1} - \varphi''_{1,1})$ [A1.7r]

Imaginary: $j_{dl}{}''_{1,1} = \omega_1 \frac{C_{dl}}{F}(\varphi'_{1,1} - \varphi^{s\,'}_{1,1})$ [A1.7i]

Overpotential

Real: $\eta'_{1,1} = \varphi^{s'}_{1,1} - \varphi'_{1,1} - \frac{dU}{dc^s} c^{s'}_{1,1}$ [A1.8r]

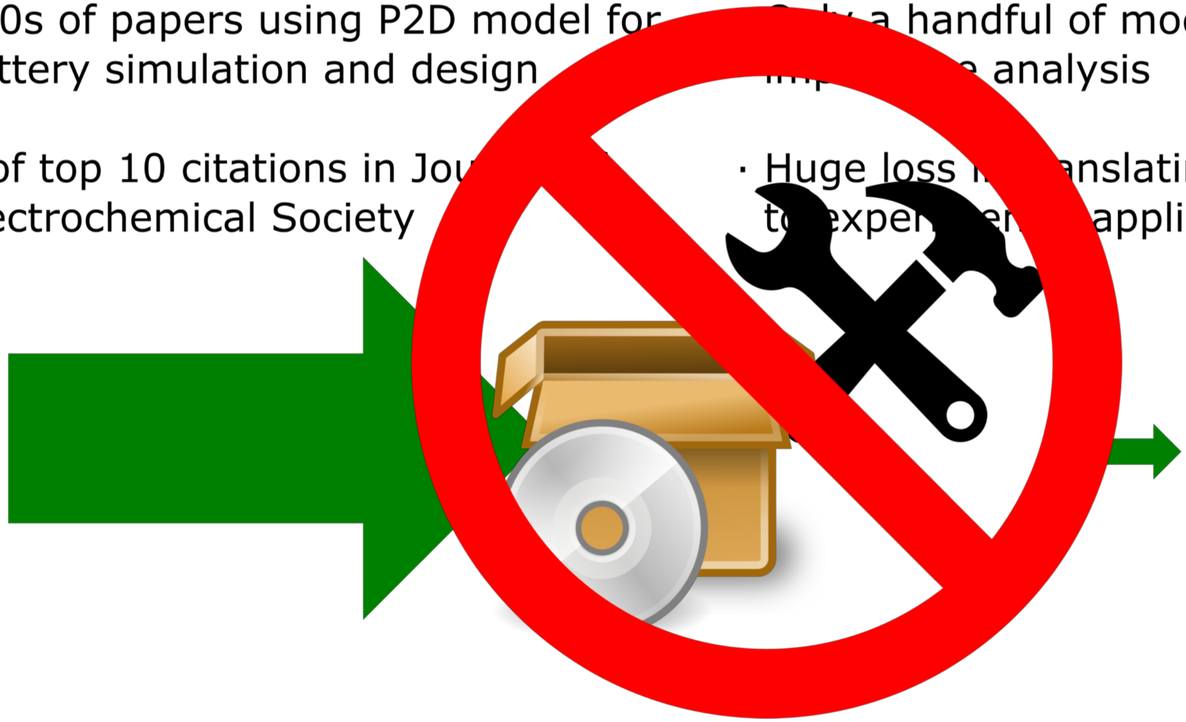
Imaginary: $\eta''_{1,1} = \varphi^{s''}_{1,1} - \varphi''_{1,1} - \frac{dU}{dc^s} c^{s''}_{1,1}$ [A1.8i]

Murbach, M.D., Schwartz, D.T. J. Electrochem. Soc. **164**, E3311–E3320 (2017)

We're missing the tools and software to make it easy

- 100s of papers using P2D model for battery simulation and design
- 3 of top 10 citations in Jou Electrochemical Society

- a handful of models ever applied to e analysis
- Huge loss anslating from modeling t exper application



M. Doyle, J. P. Meyers, and J. Newman, *J. Electrochem. Soc.*, **147**, 99–110 (2000)
Q. Guo, V. R. Subramanian, J. W. Weidner, and R. E. White, *J. Electrochem. Soc.*, **149**, A307 (2002)
G. Sikha and R. E. White, *Journal of The Electrochemical Society*, **155**, A893 (2008)
D. P. Abraham, S. Kawauchi, and D. W. Dees, *Electrochimica Acta*, **53**, 2121–2129 (2008)

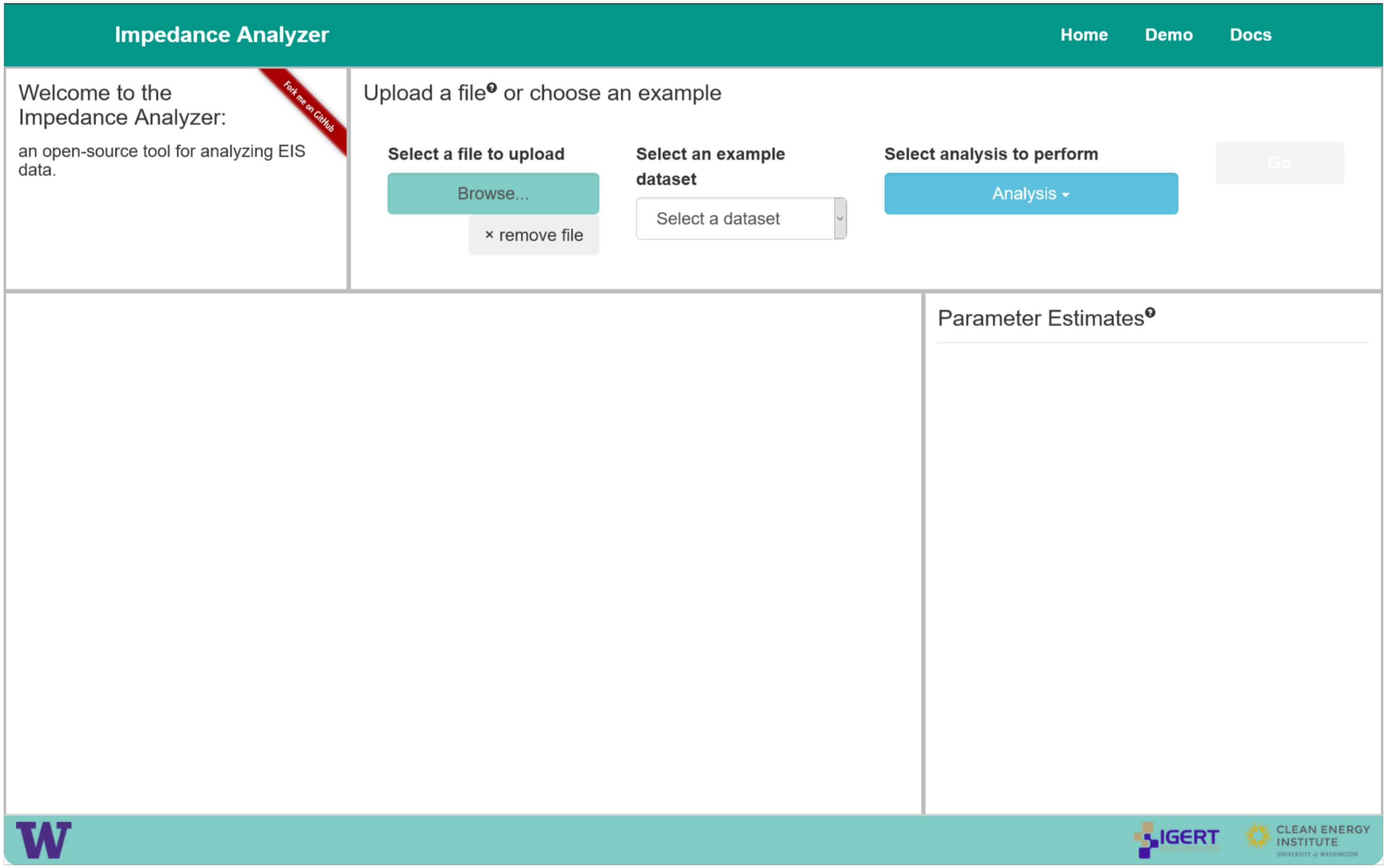
The ImpedanceAnalyzer

Goal: create a open platform for reproducible and sophisticated analysis of impedance spectra

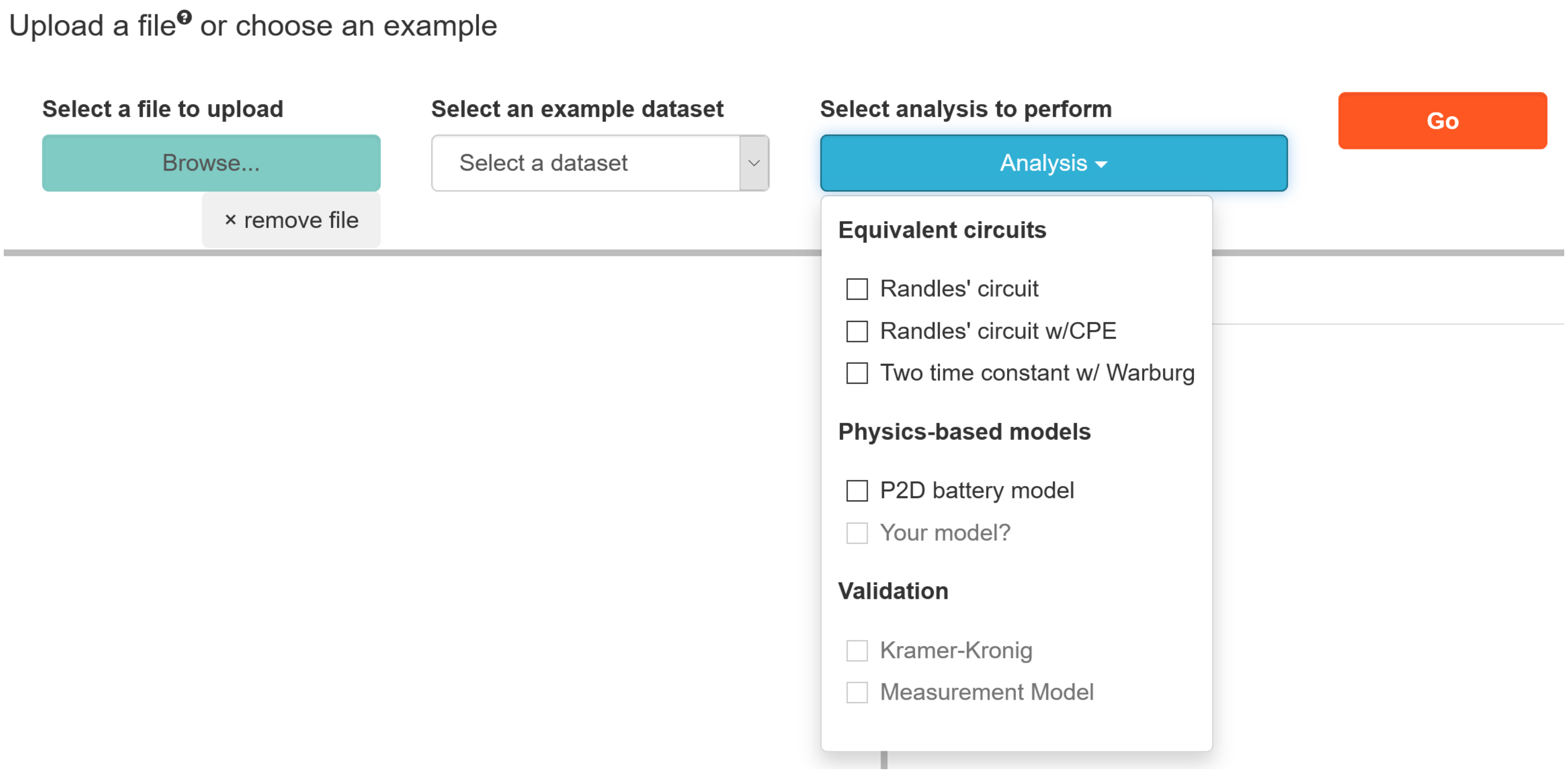
A Python backend + JavaScript frontend make sophisticated analyses and useful interactive visualizations possible

How it works:

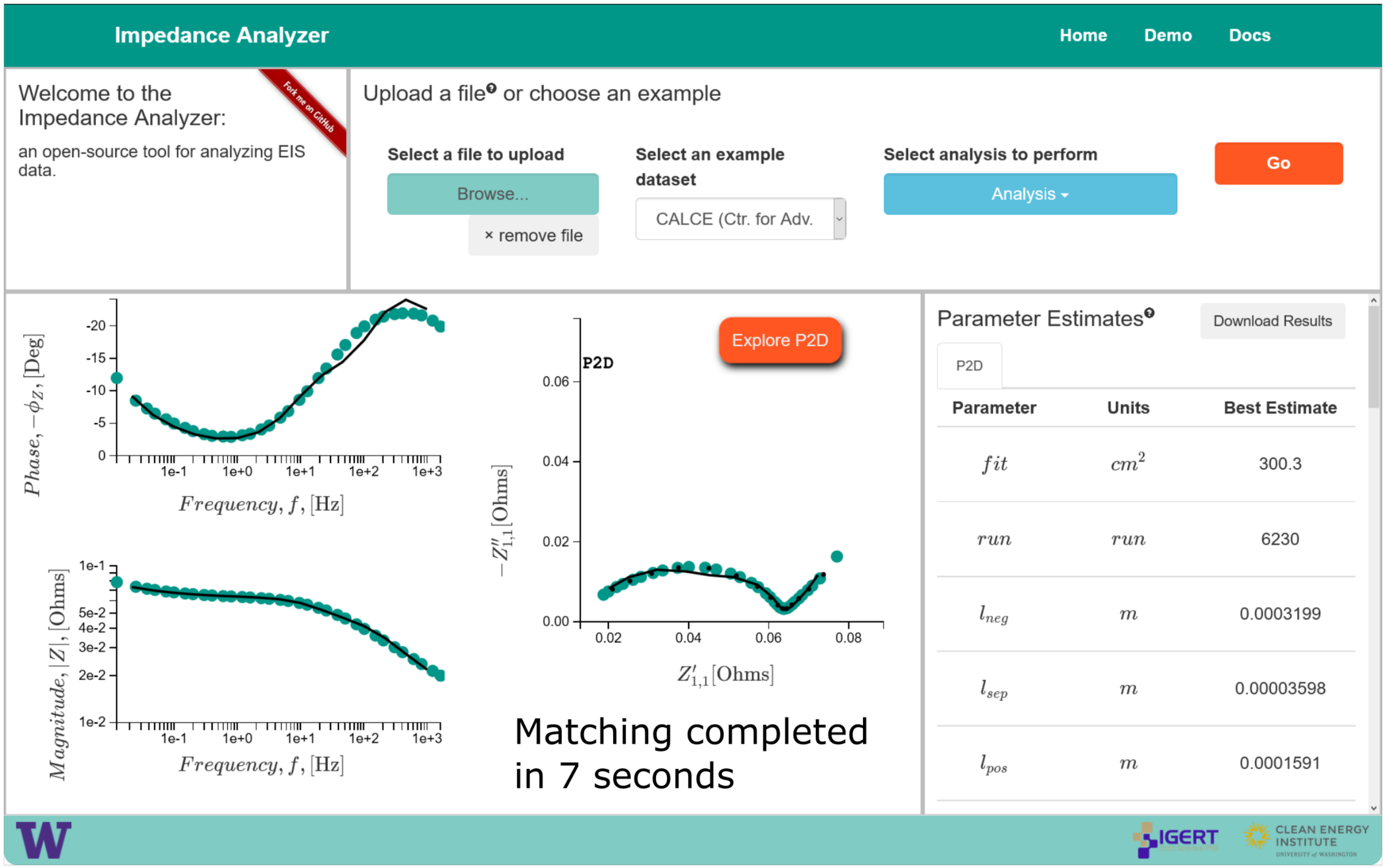
theimpedanceanalyzer.com



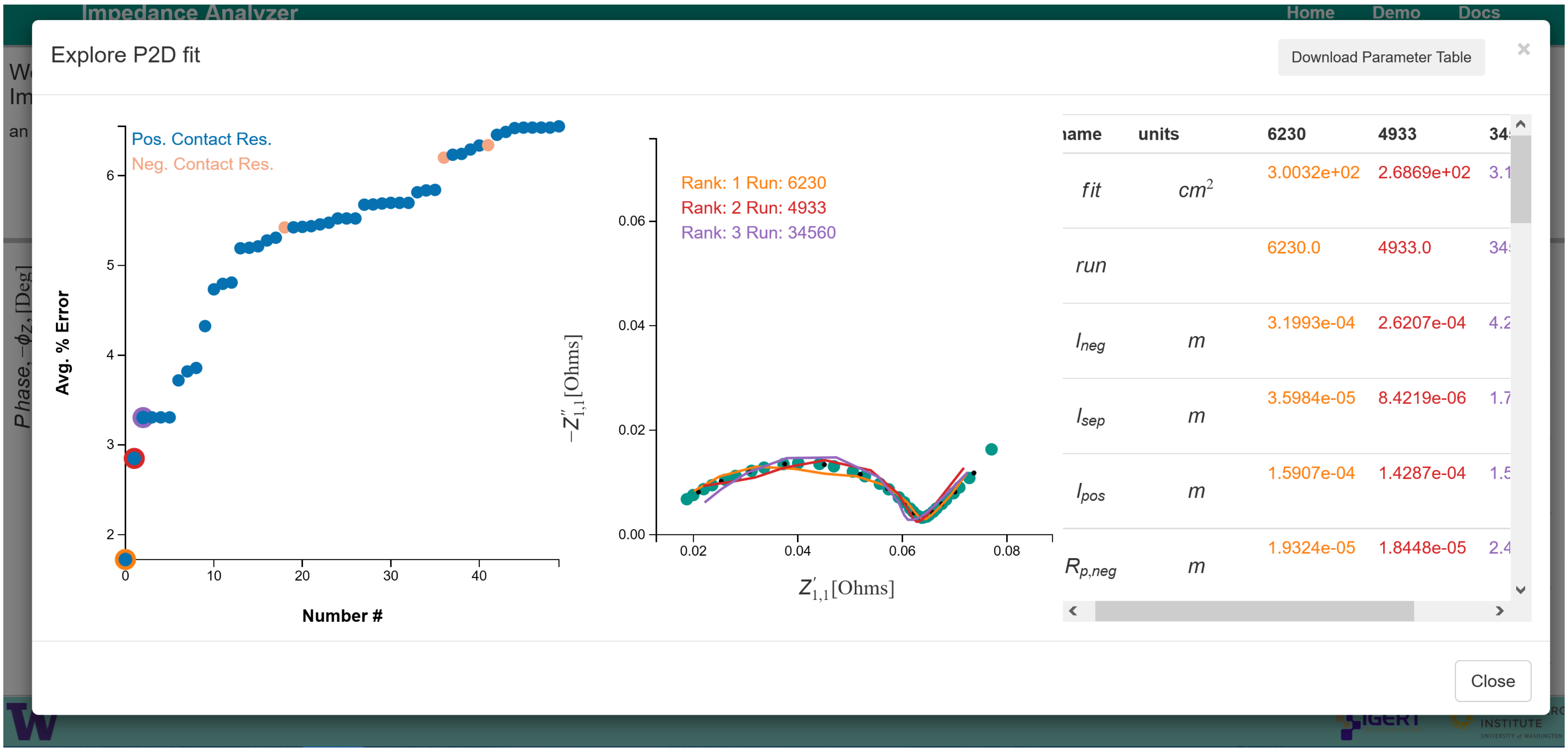
How it works: uploading data



How it works: fitting spectra



How it works: interactive visualizations



Difference in parameter estimates

Equivalent circuit methods

Randles | Randles w/CPE | Two Time Constants | P2D

Parameter	Units	Best Estimate	Error	% Error
R_0	*Ohms*	0.02360	0.001405	5.954
R_1	*Ohms*	0.03599	0.001614	4.486
C_1	*F*	0.06510	0.007915	12.16
W_1	*Ohms*	0.05633	0.02182	38.73
W_2	*Sec*	57.47	48.48	84.36

Physics-based model (P2D)

Randles | Randles w/CPE | Two Time Constants | P2D

Parameter	Units	Best Estimate
D	m^2/s	7.685e-10
$D_{s,neg}$	m^2/s	9.089e-12
$D_{s,pos}$	m^2/s	4.337e-16
$i_{0,neg}$	A/m^2	19.42
$i_{0,pos}$	A/m^2	1.556

Difference in parameter estimates

Equivalent circuit methods | **Physics-based model (P2D)**

Randles | Randles w/CPE | Two Time Constants | P2D

Randles | Randles w/CPE | Two Time Constants | P2D

<u>Ohmic Resistance:</u>

$\boldsymbol{R_0}$ = $14.3\ m\Omega$

$$\boldsymbol{R_{\Omega,P2D}} = \frac{l_{pos}}{\kappa_{e,pos} + \sigma_{e,pos}} + \frac{l_{sep}}{\kappa_{e,sep}} + \frac{l_{neg}}{\kappa_{e,neg} + \sigma_{e,neg}}$$

$$= \boldsymbol{R_{pos}} + \boldsymbol{R_{sep}} + \boldsymbol{R_{neg}} + \boldsymbol{R_{contact}} = 10.4\ m\Omega$$

<u>Mass transport:</u>

$\boldsymbol{W_1} = 98.3\ m\Omega$

$\boldsymbol{W_2} = 284.5\ sec$

$\boldsymbol{D_{s,pos}} = 4.3\text{e}{-16}\ m^2/s$

$\boldsymbol{D_{s,neg}} = 9.1\text{e}{-12}\ m^2/s$

$\boldsymbol{D} = 7.7\text{e}{-10}\ m^2/s$

$\boldsymbol{c_0} = 1485\ mol/m^3$

Open-source tools give us the opportunity to drive the field forward

- Tools is publicly available (http://www.theimpedanceanalyzer.com/)
  - Beta version. Feedback is really helpful!

- Code is on GitHub (`mdmurbach/ImpedanceAnalyzer`)
  - Use issues to suggest features
  - Pull requests for contributions
  - Star for updates

Thoughts on future features

- Integrate knowledge of known parameters
- Confidence intervals on estimated parameters
- Integrate direct, local optimization of P2D model
- …

- Add new models/physics?
- Additional UI features?

Next steps

- Building a community of electrochemical **+** data scientists
- Building a set of community developed tools for electrochemical analysis
- Building a culture valuing open datasets, open software, and impact in addition to manuscripts

Thank you!

slides at mattmurbach.com/slides