University of California, Irvine

Dynamic light scattering in electrochemical energy conversion systems

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Outline

- Brief introduction
- Overview of electrochemical energy conversion systems
- Nanoparticles size measurement using DLS
- Nanoparticles zeta potential measurements using electrophoresis
- Zeta potential as a probe of surface charge
- DLS vs streaming current/potential measurements
- Outlook
- Conclusion

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NFCRC: H_2 Hub of SoCal

In the heart of the UC Irvine campus

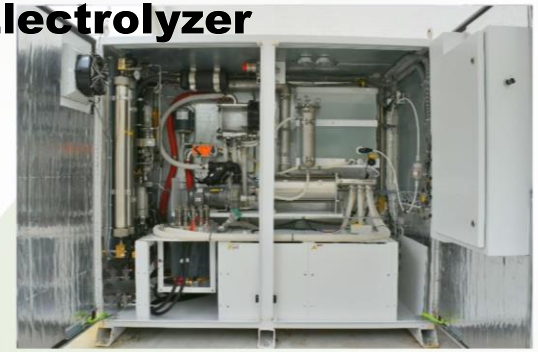
University of California, Irvine

Jack Brower, Director NFCRC

Iryna Zenyuk, Associate Director

HORIBA

Electrolyzer



Photograph of the 60kW PEM electrolyzer used in the first U.S. pilot of P2G

Hydrogen Fueling Station

FC Bus on UCI Campus

Mission: To Facilitate and to Accelerate the Development and Deployment of Advanced Power and Energy Systems

HORIBA Institute for EVs and Battery Testing

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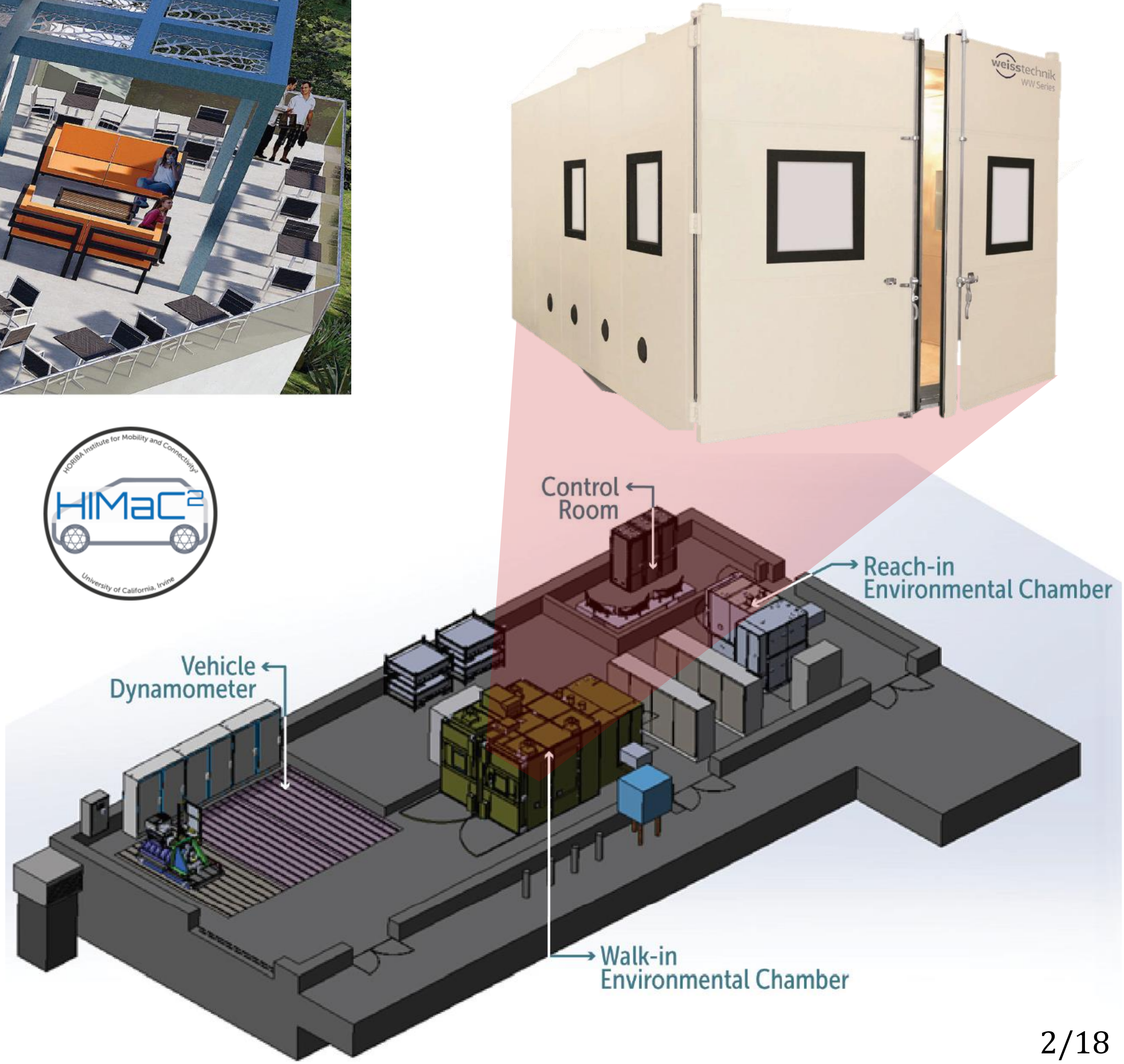
HIMaC² Laboratories

HIMaC² comprises the four following laboratories:

1. Vehicle Evolution Laboratory (VEL)
2. Grid Evolution Laboratory (GEL)
3. Connected and Autonomous Mobility Laboratory (CAML)
4. Analytic Laboratory (AL)

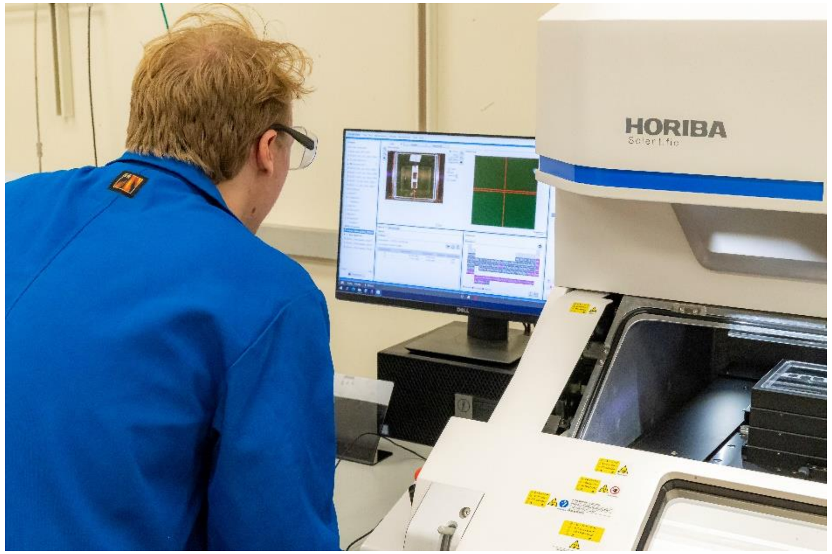
HORIBA Institute for Mobility and Connectivity²



Prof. Scott Samuelsen
Prof. Voja Stamenkovic, HIMAC director

HORIBA Analytical Lab HIMAC

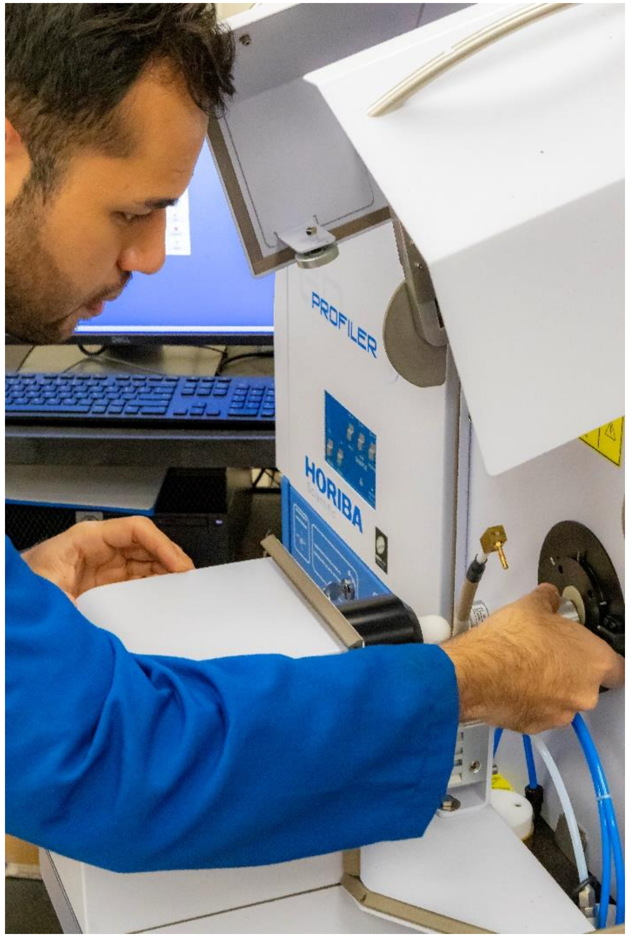
XGT-9000



John Stansberry, 3rd year Ph.D. student collecting data

SZ-100

GD Profiler 2



Devashish Kulkarni, 3rd year Ph.D. student collecting data

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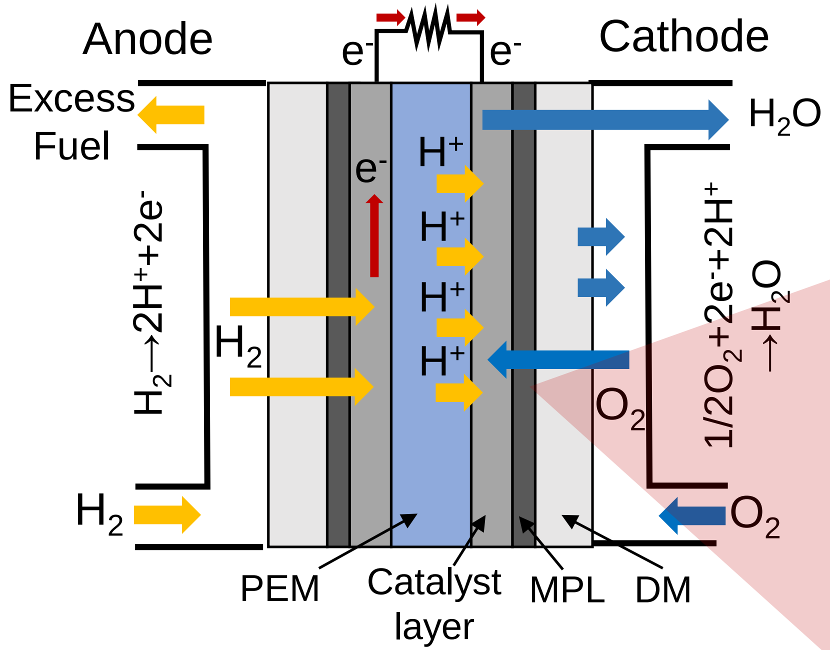
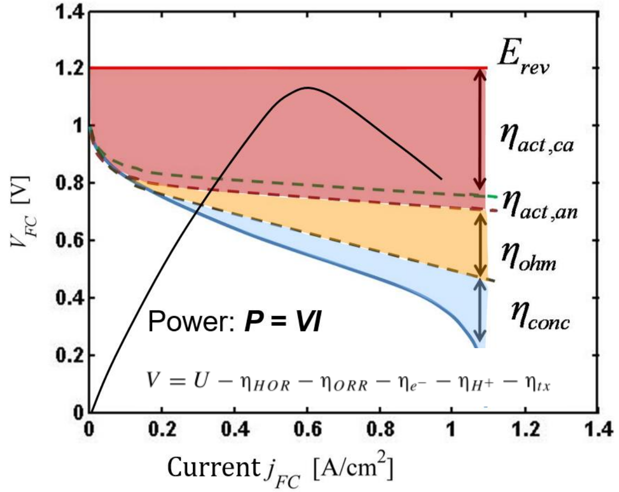
Polymer Electrolyte Fuel Cells

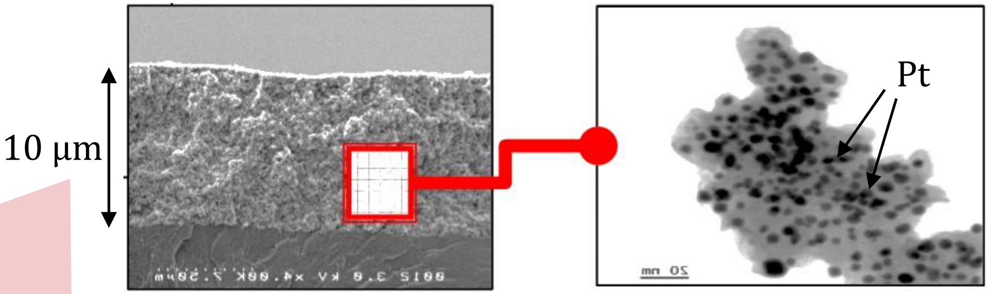
Electrode Design: reduce Cost and increase Durability

Reaction: $H_2 + 1/2O_2 \rightarrow H_2O$ + Heat + Electricity

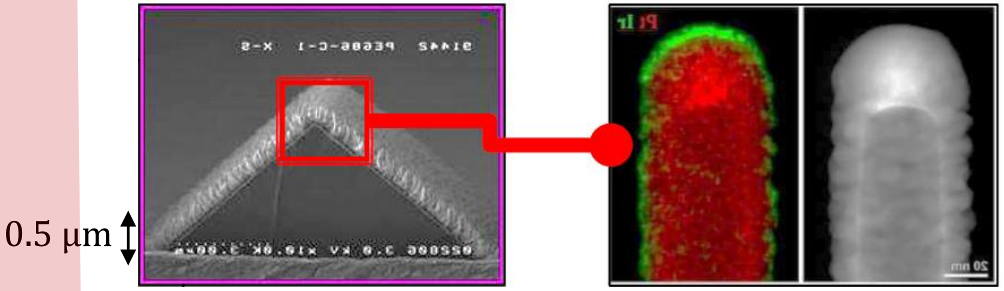




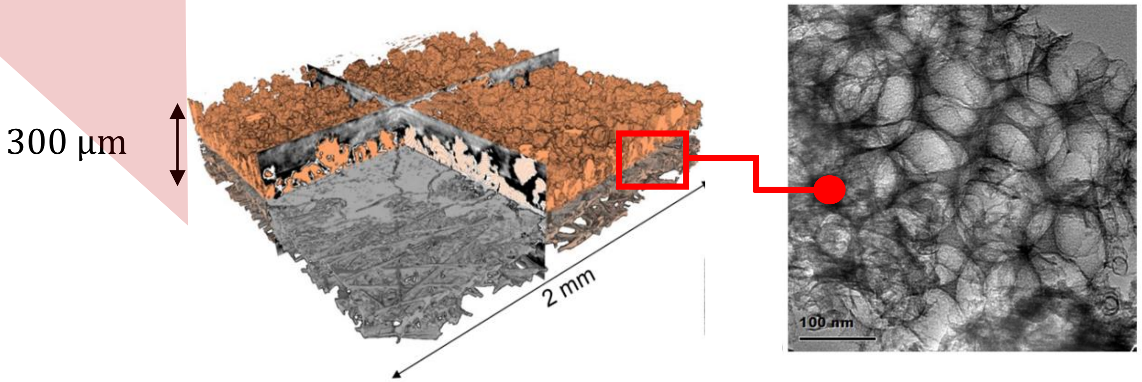
Conventional catalyst layer



Nano-structured thin-film (NSTF) electrodes developed by 3M



PGM-free electrodes



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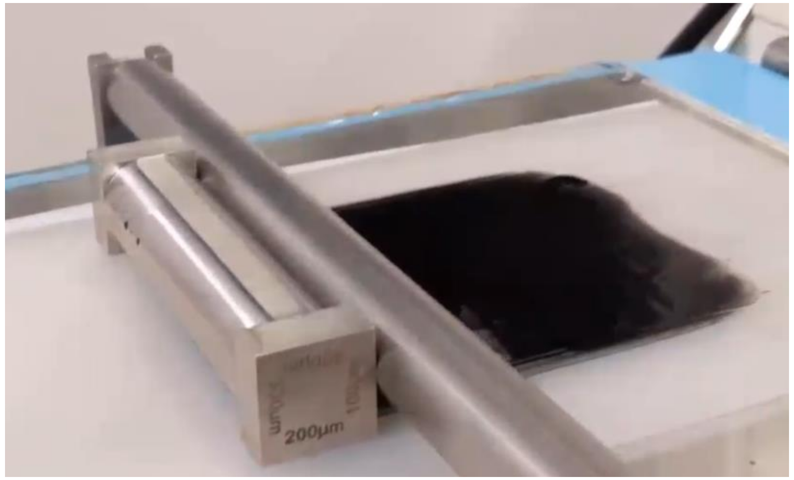
Catalyst Layer Fabrication

Combine ingredients

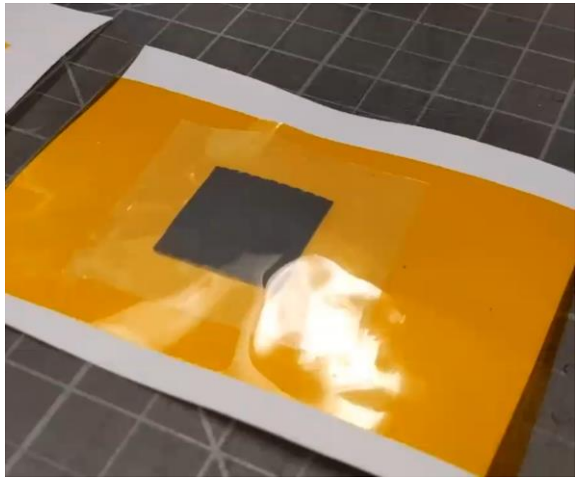
Catalyst ink

Ball-milling or spraying

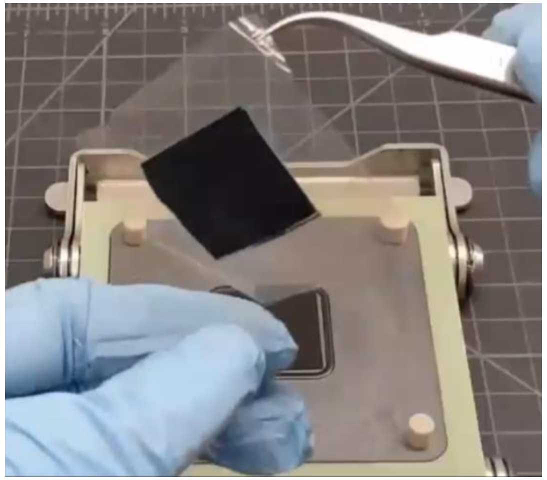
Coating



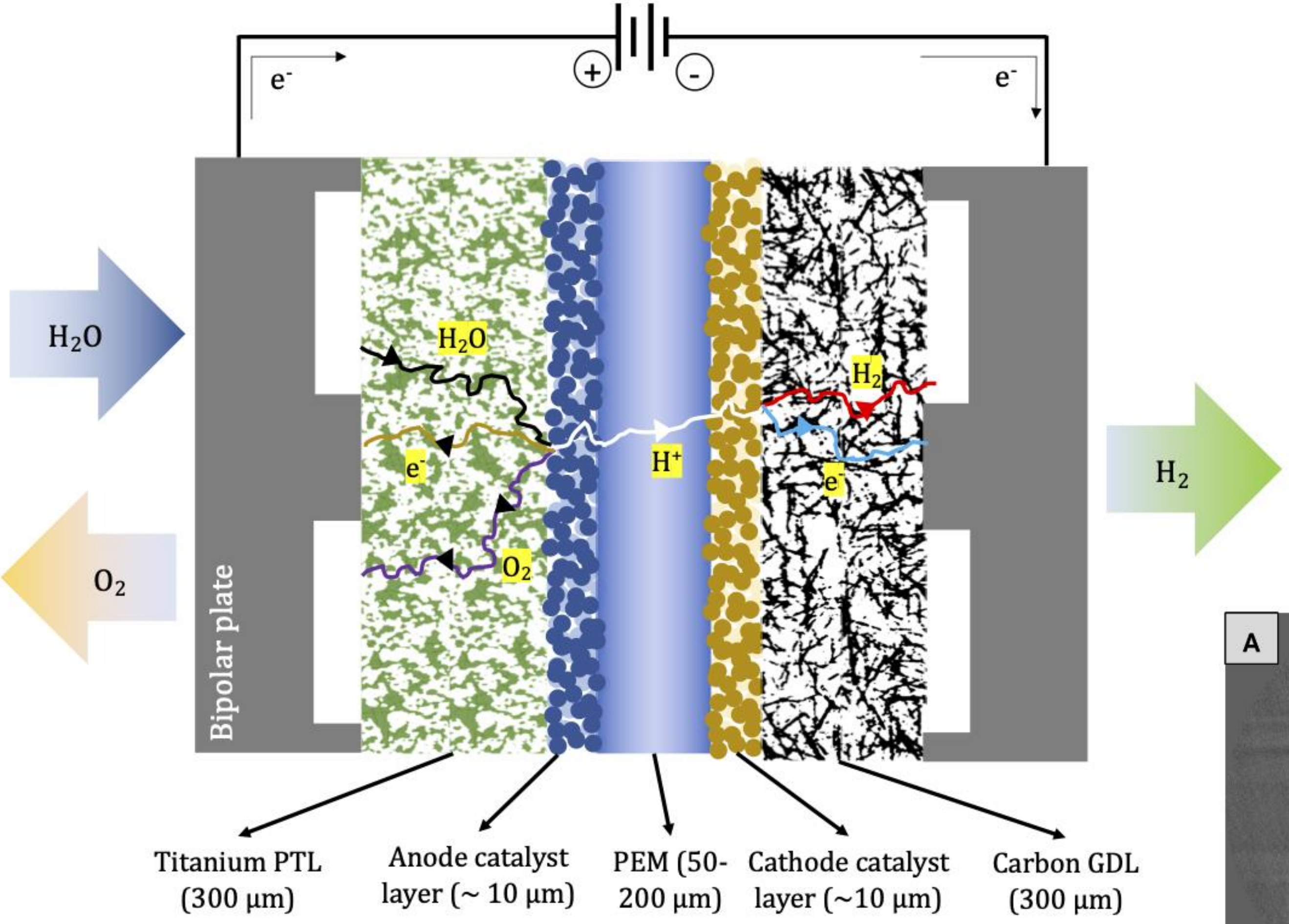
Decal hot press



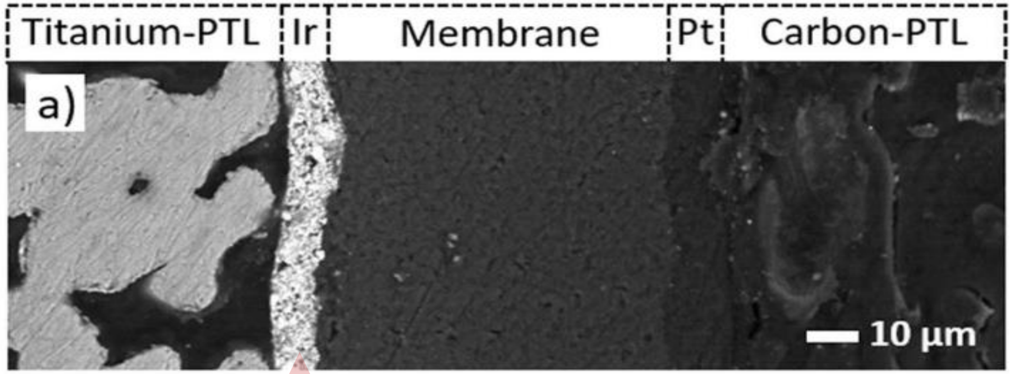
Mounting into fuel cell



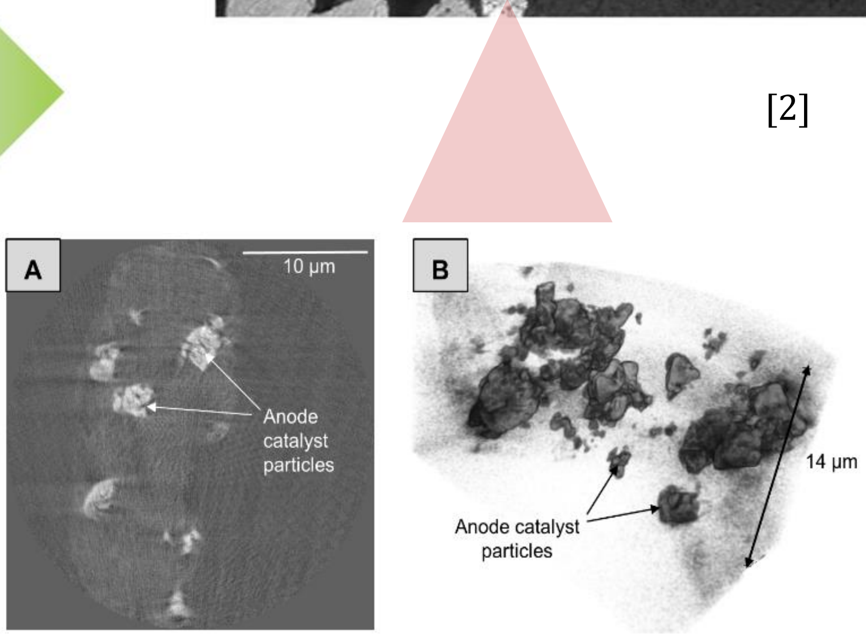
PEM Electrolyzer



[1]



[2]



1) .*Analysis of Voltage Losses and Degradation Phenomena in PEM Water Electrolyzers M. Bernt thesis,*
2). *Giner*
3) E. Leonard, A.D. Shum, D.C. Sabarirajan, N. Danilovic, C. Capuano, K. Ayers, L.M. Pant, A.Z. Weber, X. Xiao, D.Y. Parkinson, I.V. Zenyuk*, "Interfacial Analysis of PEM Electrolyzer Using X-ray Computed Tomography and Radiography", *Sustainable Energy and Fuels*, 4, 921-931, 2020

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Dynamic light scattering: nanoparticle size

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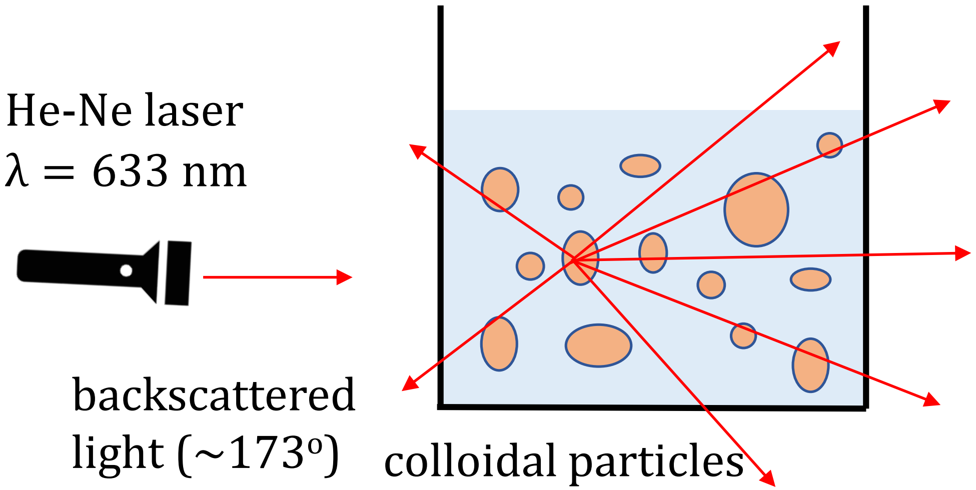
Measurement of hydrodynamic radius of particles dispersed in a solution

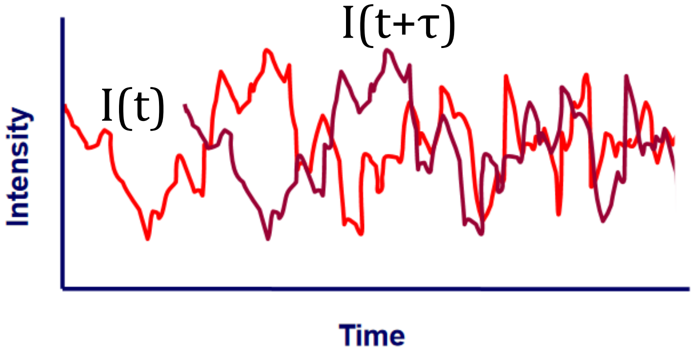
He-Ne laser
$\lambda = 633$ nm

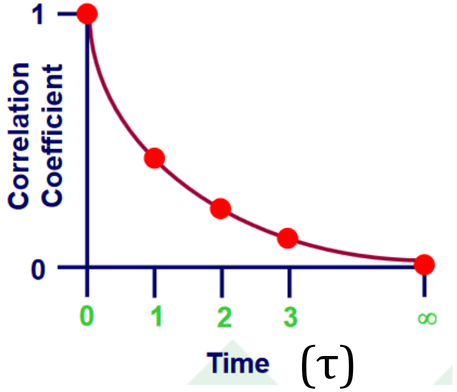


backscattered light (~173°)

colloidal particles in a dispersion

Observed Intensity vs time graph and correlation[1]





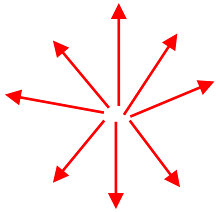
Correlation function: $G(\tau) = \left\langle \frac{I(t) \times I(t+\tau)}{I(t)^2} \right\rangle$

$G(\tau) = 1 + b.e^{-2D_t k^2 \tau}$

$|\vec{k}| = \frac{4\pi n_0}{\lambda_0 sin(\theta/2)}$

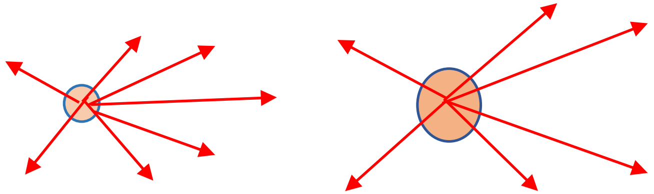
Einstein-Stokes: $R_H = \frac{k_B T}{6\pi\eta D_t}$

Rayleigh scattering



Incident laser

Mie scattering



- ❑ Elastic scattering
- ❑ very low angular dependence
- ❑ No dependence on size ($d \ll \lambda/10$)

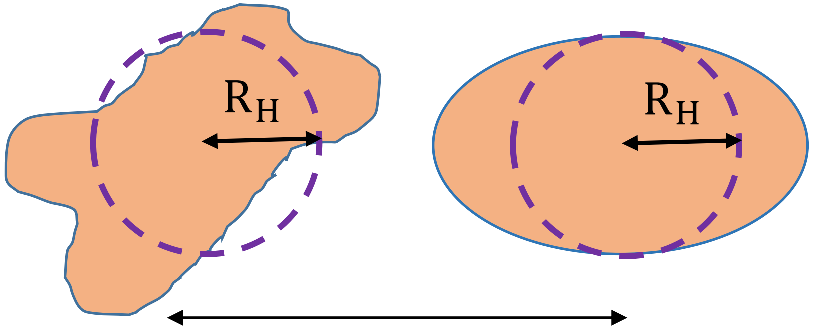
- ❑ inelastic scattering
- ❑ Intensity depends on the angle
- ❑ Intensity depends on size ($d > \lambda/10$)

[1] Bhattacharjee, Journal of Controlled Release, 2016

Dynamic light scattering: nanoparticle size

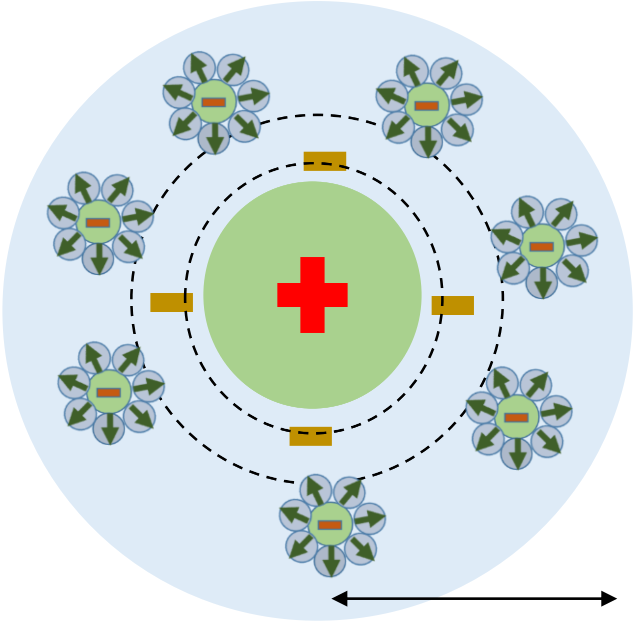
What 'size' is being measured?

Hydrodynamic radius of the particle



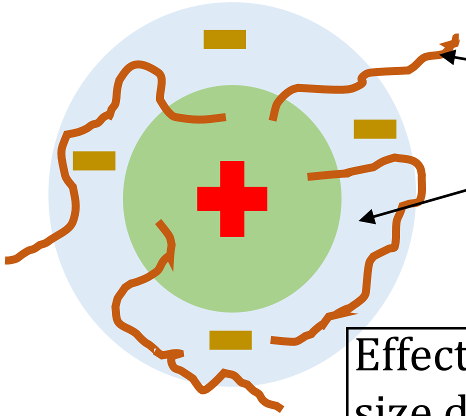
Particles of different shapes can have the same hydrodynamic radius

Size of EDL affects measurement



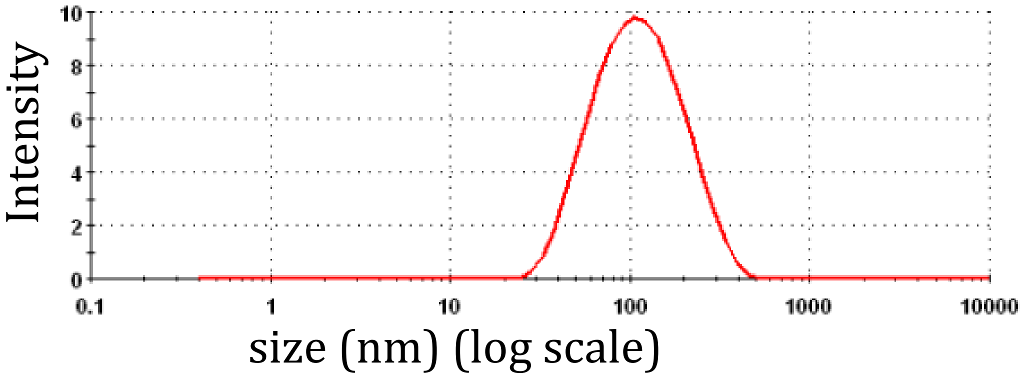
measured $R_H > a$

Colloidal particle with polymer chains



Effective hydrodynamic size depends on polymer coverage and orientation

A typical size distribution plot



DLS for PEFC catalyst and catalyst support (no ionomer)[1]

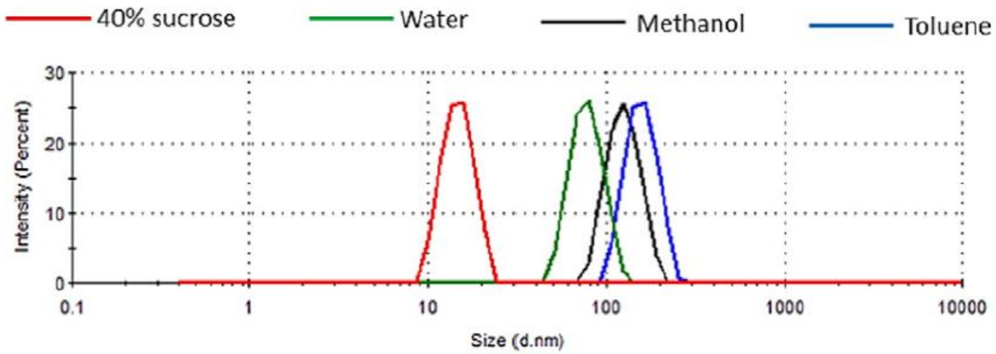
Particle	R_H(nm)	PDI	pH
Vulcan	225±20	0.41	8.3
HSC	253±38	0.66	8.9
Pt-Vul.	159±2	0.19	6.4
Pt-HSC	149±2	0.23	6.9

[1] Khandavali et al, ACS App. Mater. Interfaces, 2018

Dynamic light scattering: nanoparticle size

Effects of chemical composition of the solution

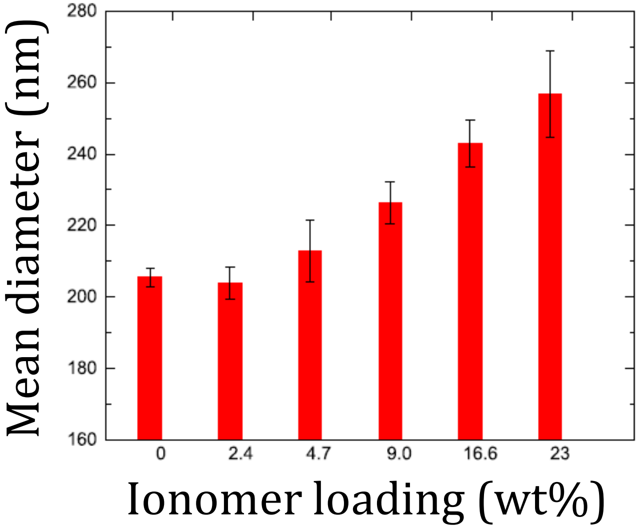
Size distribution of carbolxylated latex beads in different background solutions[1]

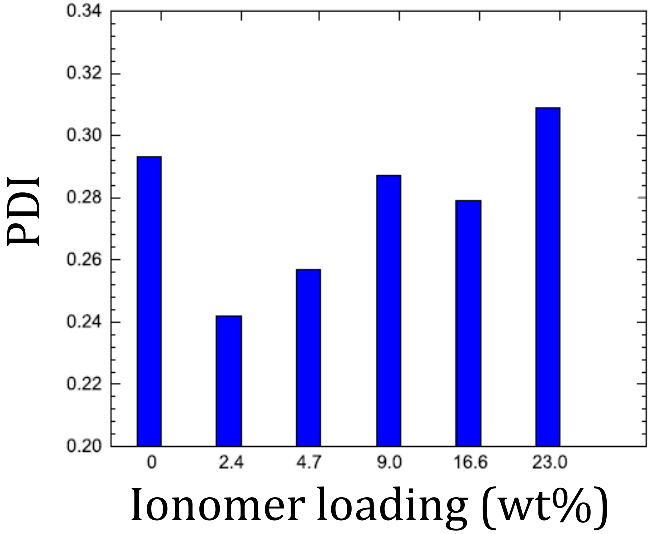


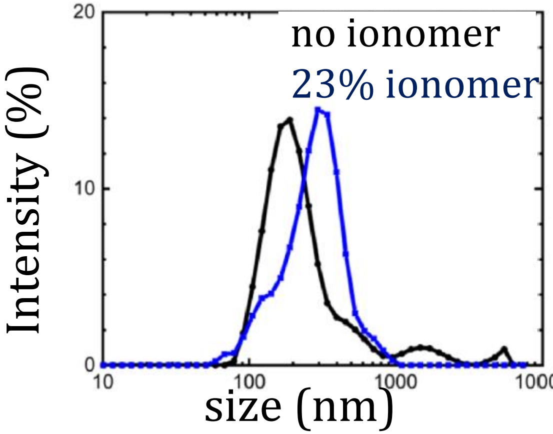
Solvent	Viscosity (cP)	RI	z-average (nm)	PDI
40% sucrose	5.1178	1.4	15	0.008
water	0.8872	1.33	87	0.009
methanol	0.5476	1.326	122	0.011
toluene	0.5564	1.496	153	0.005

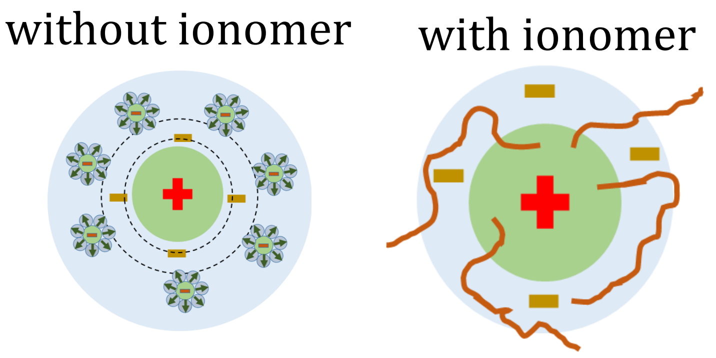
commercially available carboxylated latex beads concentration- 100 μg/ml, Temp- 25 C

PEM electrolyzer anode: IrO_2 catalyst particle size in solutions with different ionomer loadings[2]









[1] Bhattacharjee, Journal of Controlled Release, 2016

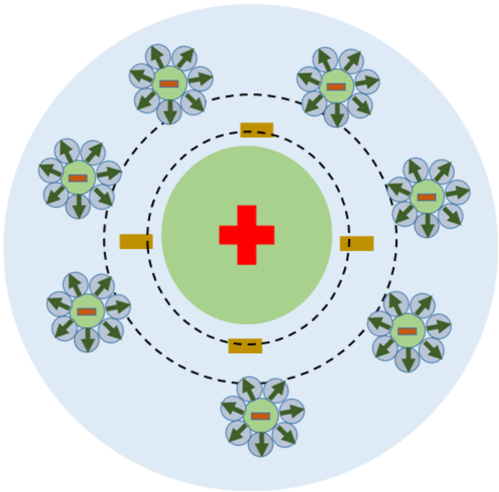
[2] Khandavali et al, ACS App. Mater. Interfaces, 2019

Dynamic light scattering: nanoparticle size

Size of particles measured by different techniques

DLS: particles moves with its EDL

Electron microscopy: scattering from electron-dense region[1]



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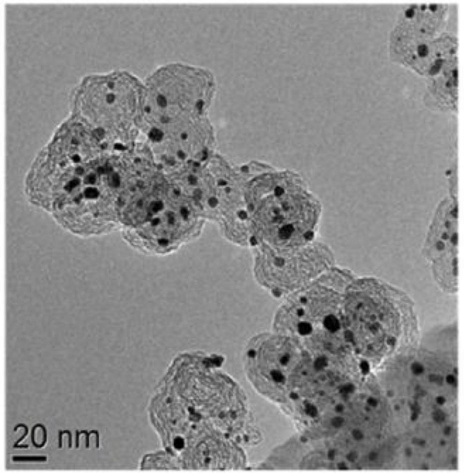
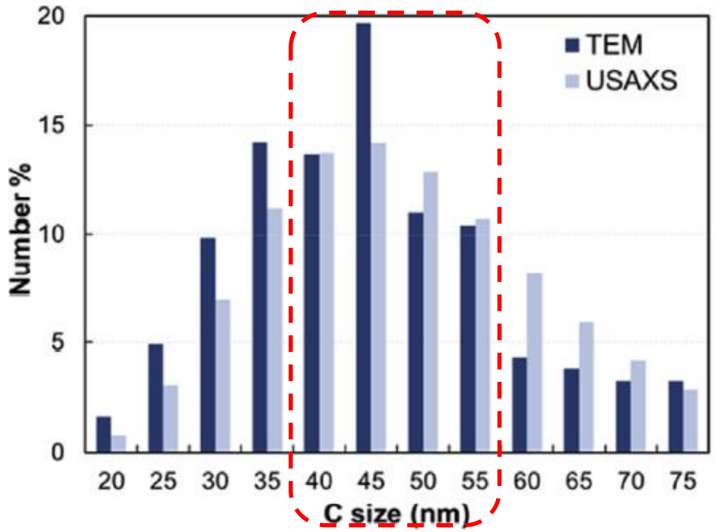


Transmission electron micrograph of Pt/C (40%) with ionomer (I/C ~ 1)



TEM vs USAXS of Pt/C (HSC)

USAXS = Ultra small angle Xray scattering (0.1 – 10°)

$$1.2 \times 10^{-4} < |\vec{k}| < 0.28\ A^{o\,-1}$$

- ❑ Particle is surrounded by solvated ions
- ❑ Dilute solution ⇒ large Debye length
- ❑ Electronic structure does not impact
- ❑ Does not relate to 'dry' environment

[1] Cetimbas et al, Journal of Power Sources, 2017

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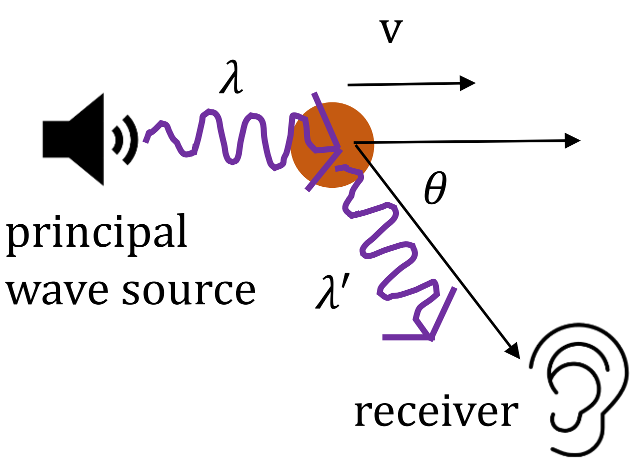
Electrophoretic light scattering: zeta potential

Measurement of zeta potential of nanoparticles in a colloidal dispersion

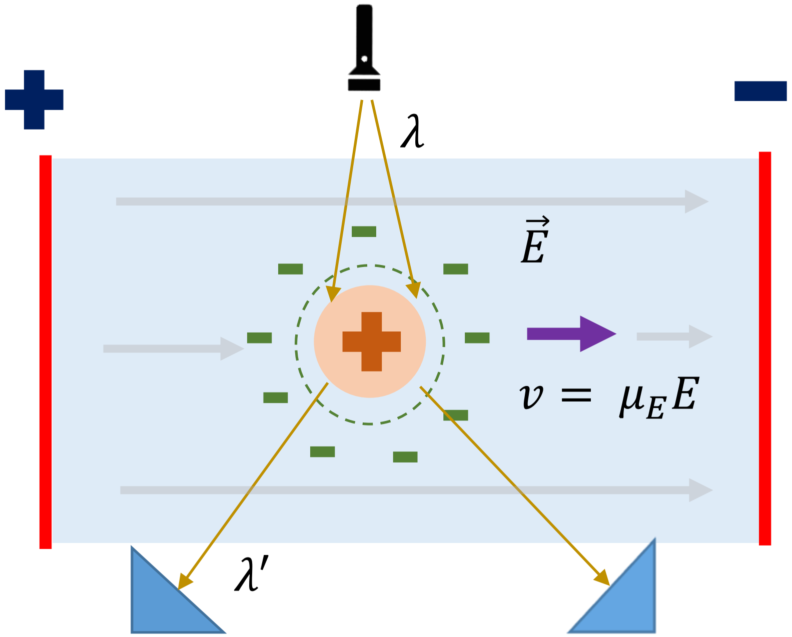
Doppler effect: change in frequency due to relative motion between source and the observer



$$\lambda' = \left(1 - \frac{v\,cos\theta}{c}\right)\lambda$$

scatterer acts as the secondary wave source

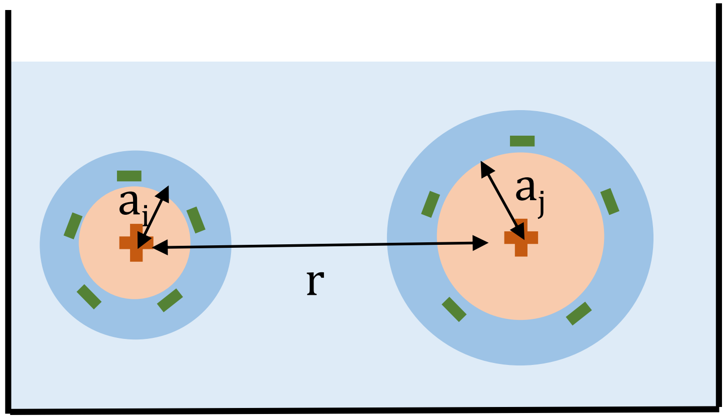
Electrophoretic light scattering



Henry's equation: $\frac{v}{E} = \frac{2}{3}\frac{\epsilon_r\epsilon_0}{\eta}\zeta\, f\left(\frac{a}{\lambda_D}\right)$

for $\frac{a}{\lambda_D}$ >>1, f($\frac{a}{\lambda_D}$)=3/2 (Smoluchowski)

Interaction energy: Derjaguin-Landau-Verwe-Overbeek (DLVO)[1]



$$U = -\frac{A}{6}\frac{a_i a_j}{(a_i+a_j)}\frac{1}{r-(a_i+a_j)} + 4\pi\epsilon_o\epsilon_r\ \zeta^2\ \frac{(a_i+a_j)^2}{r}$$

van der Waals
Derjaguin approx.
a >> gap between spheres

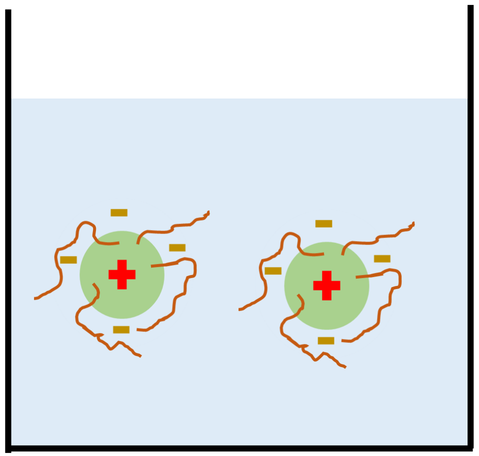
Coulomb repulsion

A = Hamaker constant
(dielectric constant, refractive indices)
There are different versions of vdW eqn

Electrophoretic light scattering: zeta potential

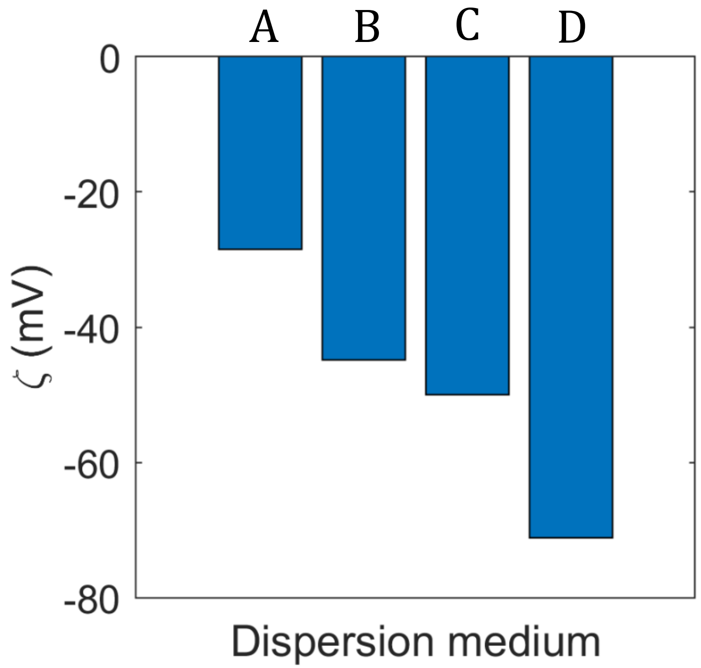
Determining catalyst ink stability from zeta potential

Ink in different media



Ink recipe:
Vulcan XC 72R in dispersion
Ionomer (I/C ~1)
Different dispersion media

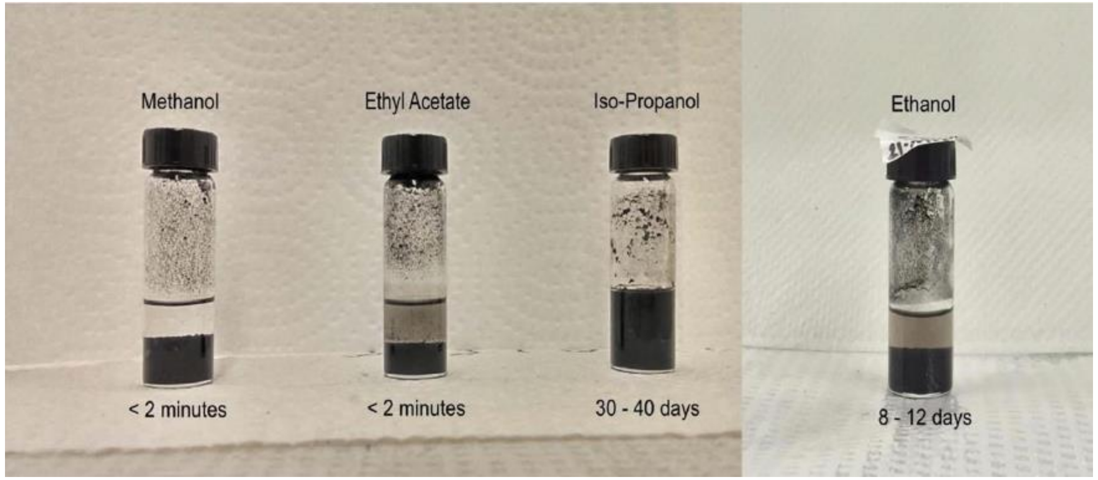
Catalyst ink stability: choice of dispersing medium (no ionomer)[1]



Important criterion:
zeta potential should be higher

Choice based on zeta potential analysis: Isopropanol

Catalyst ink stability: visual analysis[2]
dispersion with low zeta sediments faster



A- methanol
B- ethanol
C- ethyl acetate
D- isopropanol

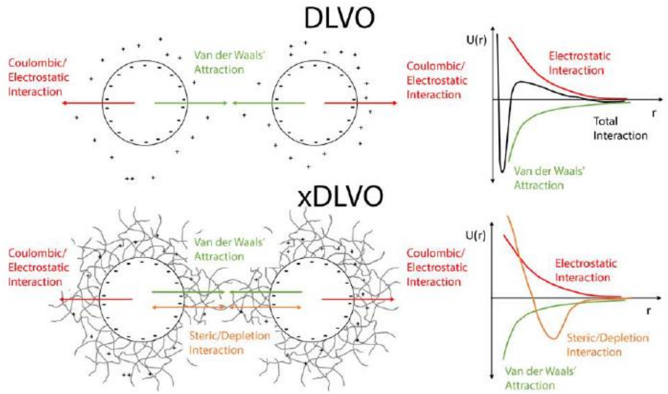
Choice based on visual stability analysis: Isopropanol

[1] Xu et al, Carbon 2007
[2] Shukla et al, Journal of Electrochem. Soc, 2017

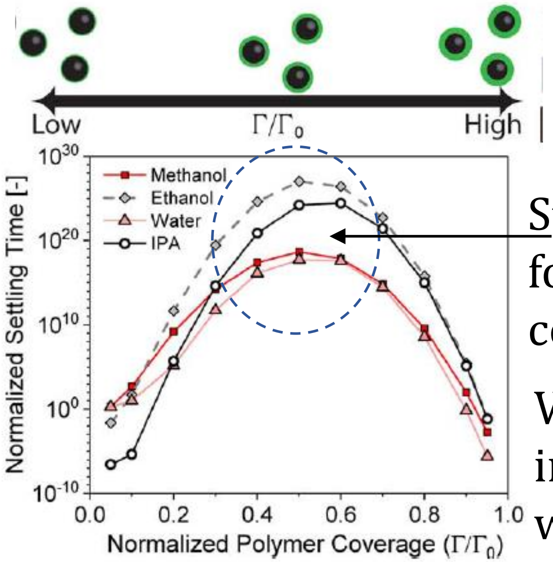
Electrophoretic light scattering: zeta potential

Zeta potential and ink stability in catalyst inks in presence of ionomer

Effect of ionomer on ink stability (Vulcan XC 72R)[1]



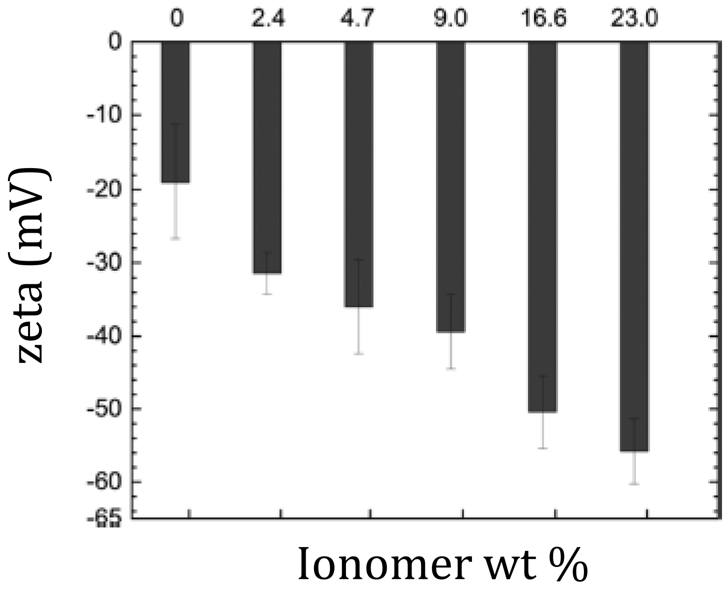
Addition of ionomer adds steric repulsion between the particles. Hence more stability is expected

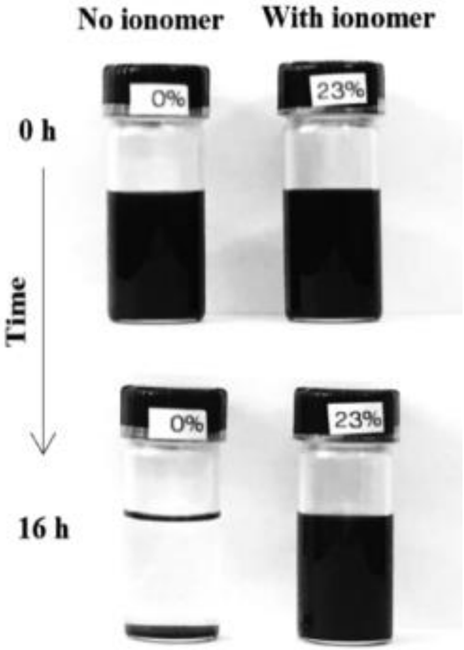


Stability maximum for ionomer coverage ~0.5

Vulcan carbon in dispersion with ionomer

Effect of ionomer on ink stability (IrO_2)[2]





**Decreasing zeta most likely due to adsorption of SO_3H^- group

[1] Dixit et al, Journal of Electrochem. Soc, 2018
[2] Khandavali et al, ACS App. Mater. Interfaces, 2019

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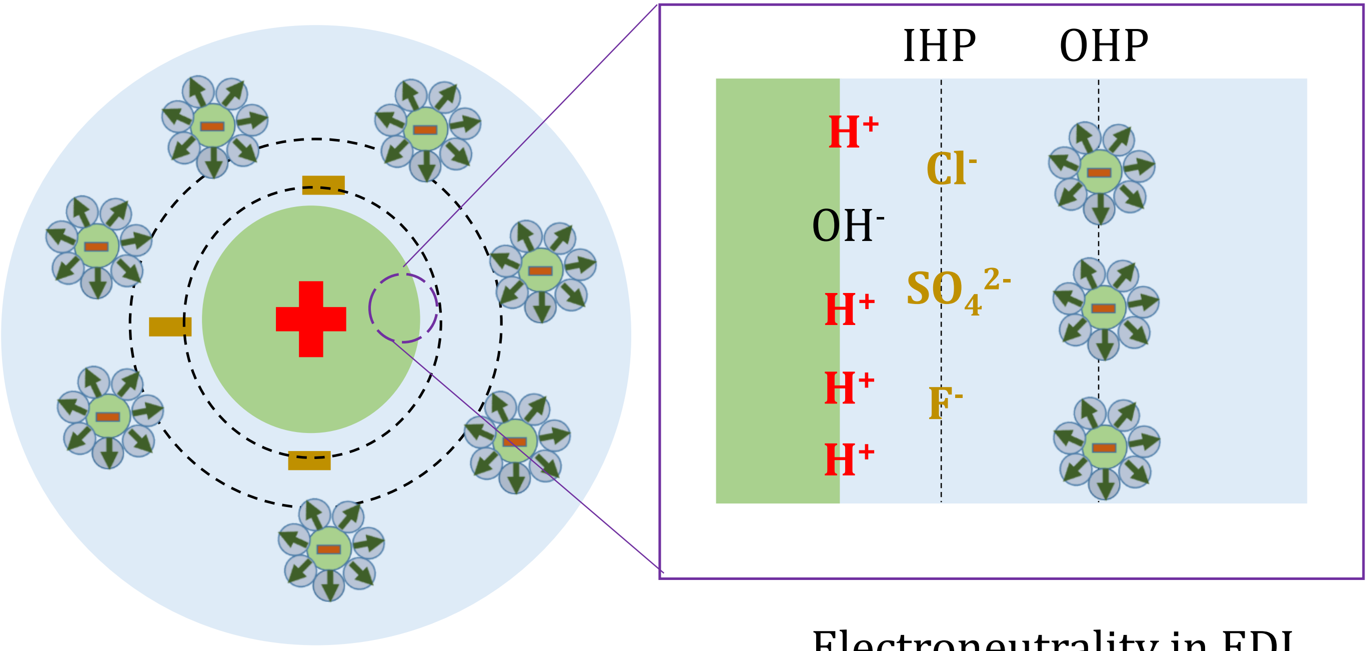
Electrophoretic light scattering: zeta potential

Zeta potential and its variation with chemical composition

Charging at a solid-electrolyte interface



When no potential is applied on solid, charging occurs due to adsorption and desorption of ions present in the electrolyte. In aqueous solution, H^+ and OH^- are principal charge determining ions

Electroneutrality in EDL

$$\sigma_{ox} + \sigma_{IHP} + \sigma_{diff} = 0$$

Site-binding equilibria[1]

$$MOH_2^+ \rightleftharpoons MOH + H^+ \quad K_{a_1}$$

$$MOH \rightleftharpoons MO^- + H^+ \quad K_{a_2}$$

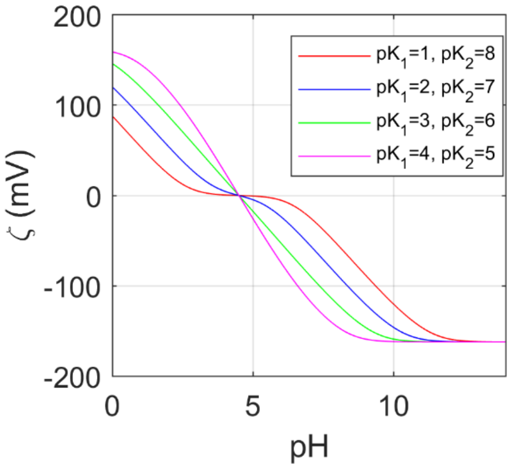
Analytical prediction and experimental results

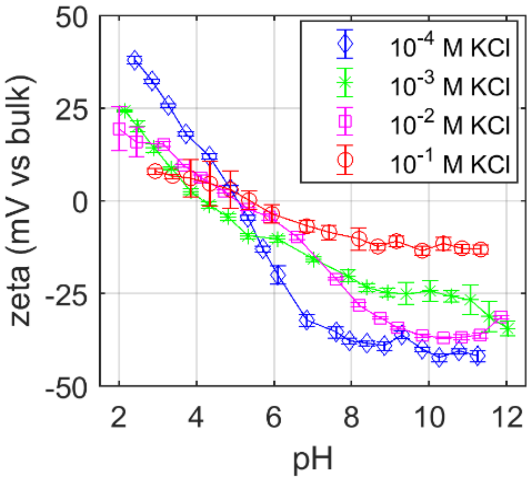
applied to polycrystalline Au-electrolyte[2]

$$[MOH_2^+] = [MOH] c_{H^+}^{bulk} \exp\left(-\frac{e\zeta}{k_B T}\right) 10^{pK_1}$$

$$[MO^-] == 10^{-pK_2}[MOH] \frac{\exp\left(\frac{e\zeta}{k_B T}\right)}{c_{H^+}^{bulk}}$$

$$\sigma_d = -\left(8 k_B T \epsilon_r \epsilon_0 n^{bulk}\right)^{\frac{1}{2}} \sinh\left(\frac{e\zeta}{2 k_B T}\right)$$





[1] Yates et al, Journal of Chemical Soc., 1974

[2] Saha et al, Journal of Electrochem. Soc, 2021 (under review)

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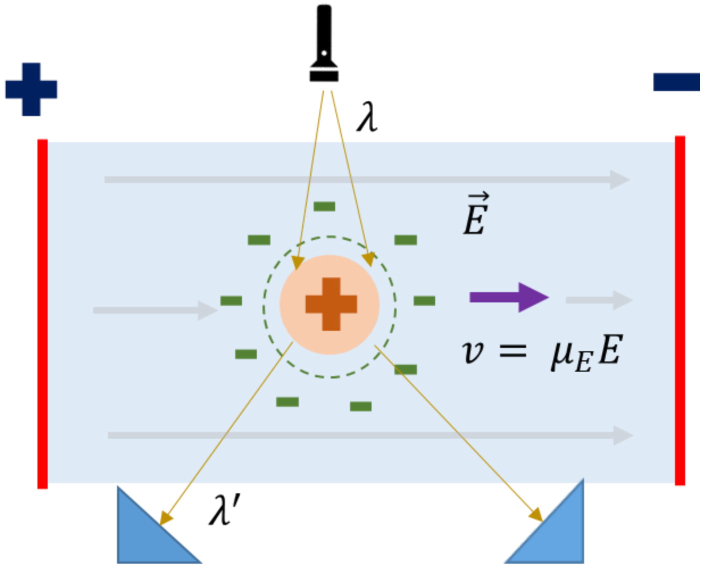
- ❖ Conclusion

Electrokinetics techniques: zeta potential

Zeta potential measured by various techniques

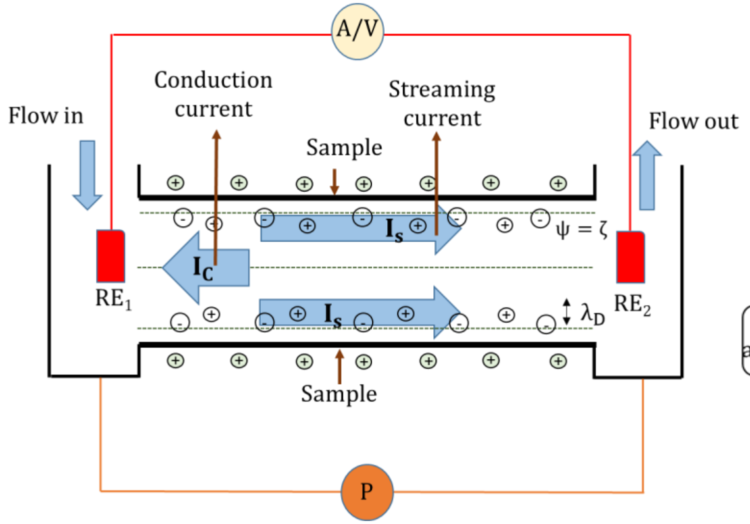
Electrophoretic light scattering



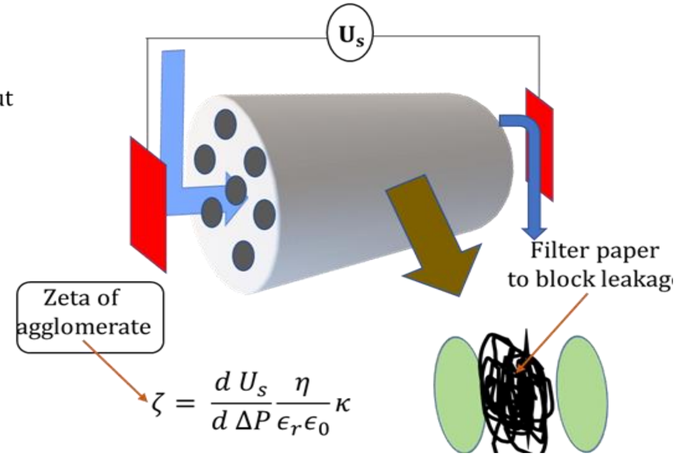
Henry's equation: $\frac{v}{E} = \frac{2}{3}\frac{\epsilon_r\epsilon_0}{\eta}\zeta f\left(\frac{a}{\lambda_D}\right)$

- ❑ Works for electrolytes with similar ionic mobilities (KCl)
- ❑ Works well in dilute solution
- ❑ Titration is time consuming

Streaming current/potential



macroscopic planar solid (~ cm^2)



macroscopic granular solid irregular geometry (~ cm^2)

Modified Helmholtz-Smoluchowski Eqn[1] $\frac{d}{dP}\begin{bmatrix} I_S \\ U_S \end{bmatrix} = \zeta\frac{\epsilon_r\epsilon_0}{\eta}\begin{bmatrix} A/L \\ 1/\kappa \end{bmatrix}$

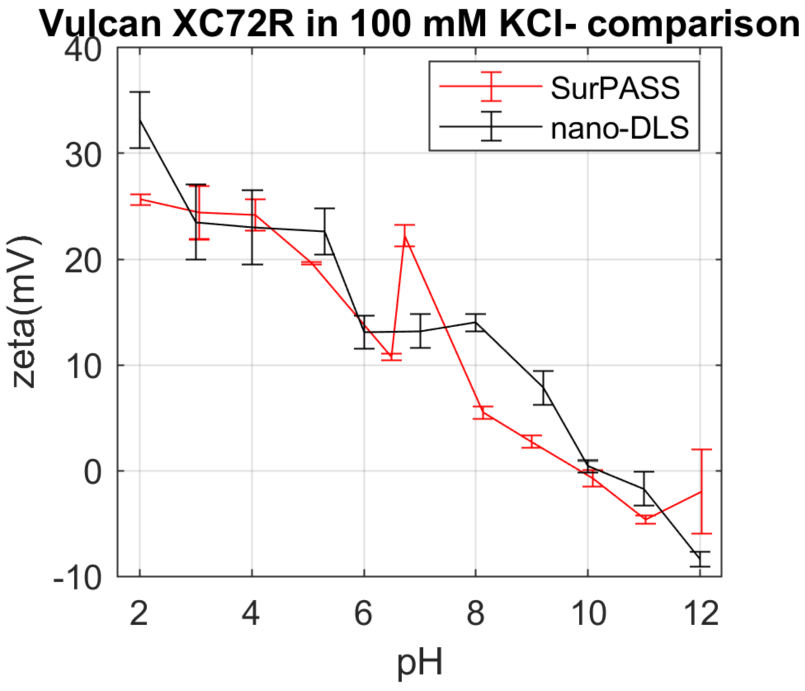
- ❑ Experimental technique flexible for different geometries
- ❑ For conductive samples, streaming current is convenient
- ❑ Flexible across choice of electrolytes
- ❑ **Can apply potential on the sample and study charging behavior**

[1] Werner et al, Journal of Colloid & Interfac. Sci., 1998

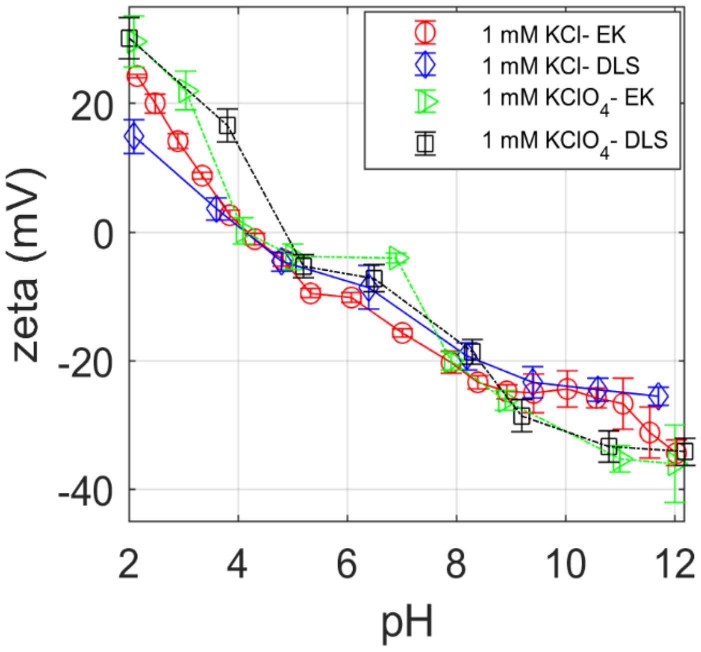
Electrokinetic techniques: zeta potential

Equivalence between DLS and streaming current/potential

For Vulcan XC 72R[unpublished]



For polycrystalline Au[1]



Equivalence between DLS and streaming current/potential established for the first time

[2] Saha et al, Journal of Electrochem. Soc, 2021 (under review)

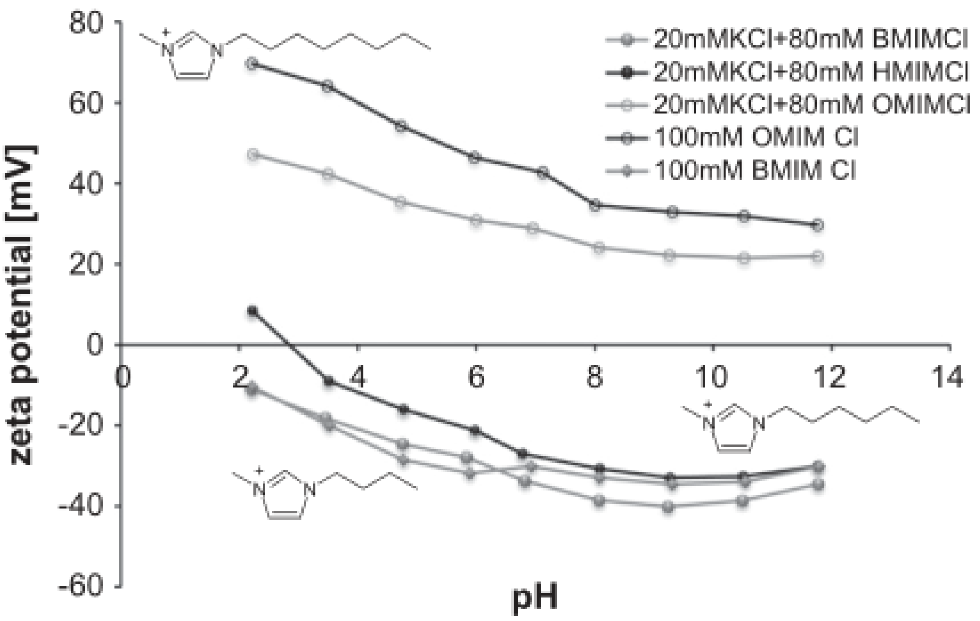
Outline

- ❖ Brief introduction
- ❖ Overview of electrochemical energy conversion systems
- ❖ Nanoparticles size measurement using DLS
- ❖ Nanoparticles zeta potential measurements using electrophoresis
- ❖ Zeta potential as a probe of surface charge
- ❖ DLS vs streaming current/potential measurements
- ❖ **Outlook**
- ❖ Conclusion

Outlook and Limitations

Outlook: zeta potential in ionic liquid

Interaction at solid-ionic liquid interface is not very well understood



zeta vs pH of kaolinite in ionic liquid[1]

- ❑ Imidazolium cations get adsorbed on the solid makes zeta potential positive
- ❑ May have significant consequences for fuel cells

Limitations of light scattering technique

- ❑ Measures effective size of the particle, not actual
- ❑ Principle limitation is the concentration of electrolyte. Light scattering technique works only with dilute electrolytes
- ❑ Electrophoresis requires using an electrolyte which has almost same mobilities (diffusion constant) for the cation and the anion. This poses restrictions on the choice of electrolytes
- ❑ Can't apply potential and measure zeta potential

[1] Markiewicz et al, Chemosphere, 2013

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Conclusions

Size measurement

- DLS enables measurement of nanoparticle agglomerates in a colloidal dispersion
- Shows how agglomeration phenomena are related to the particle-solvent interaction
- Works well in dilute solutions
- Gives an estimate of hydrodynamic size
- Size includes the particle + EDL. Other size determination techniques like electron microscopy produces different results

Zeta potential measurement

- Zeta potential of nanoparticles in a dispersion reveals surface charge of the particles
- Dispersion with a higher values of zeta potential implies higher stability. Implies higher shelf life catalyst inks.
- DLVO theory can successfully explain the stability. Problems arises when ionomers are present. Several extended DLVO models have been proposed
- An optimum ionomer coverage reveals high zeta potential and higher stability
- Adsorption of ionic liquid on nanoparticles can be studied by zeta potential measurement

University of California, Irvine

Thank You!