Improving performance of electrocatalysts by ionic liquid modifications

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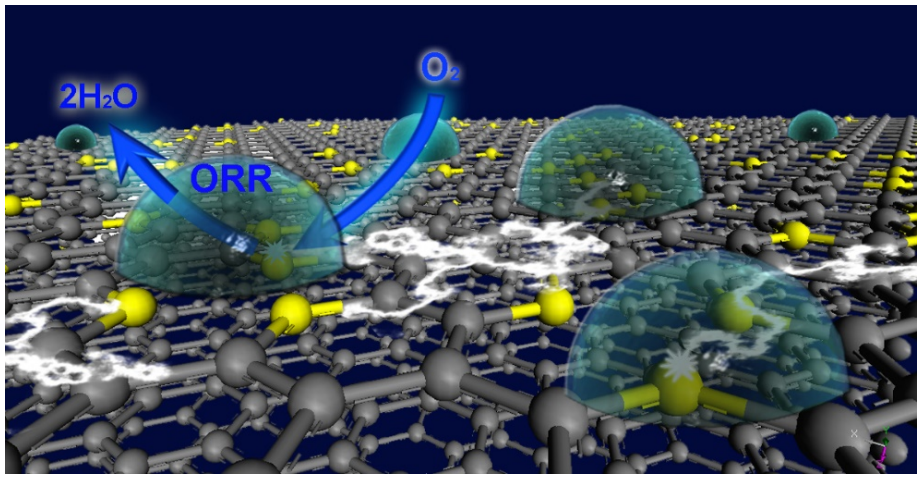
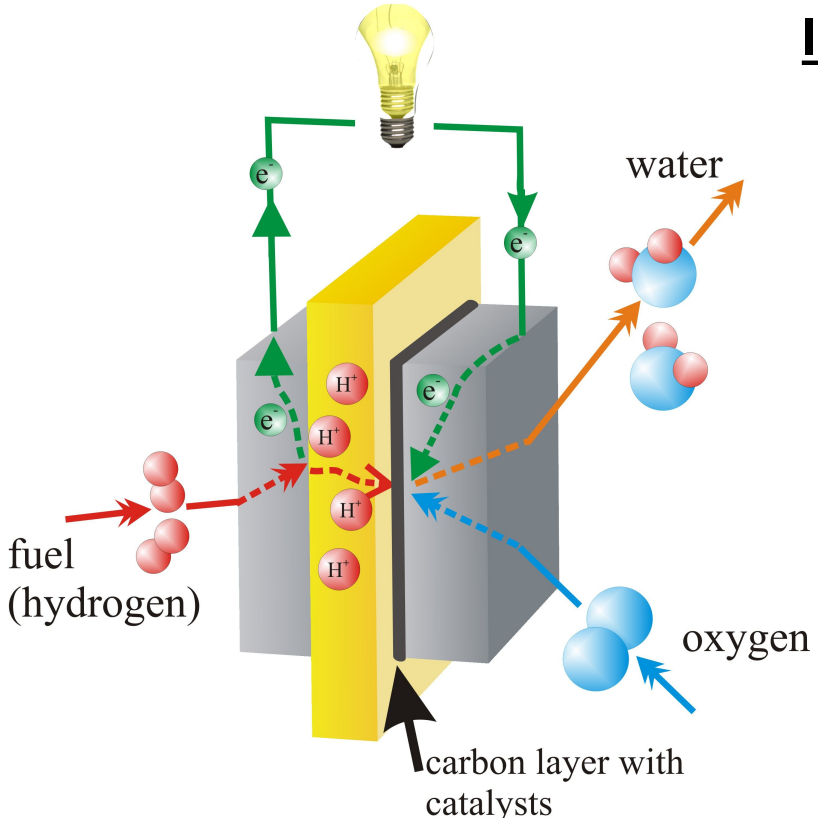


Background



Drawbacks

High Cost & Limited Stability

Increasing demand on Zero Emission Vehicles

Germany: latest in **2030**, only zero-emission vehicles will be approved

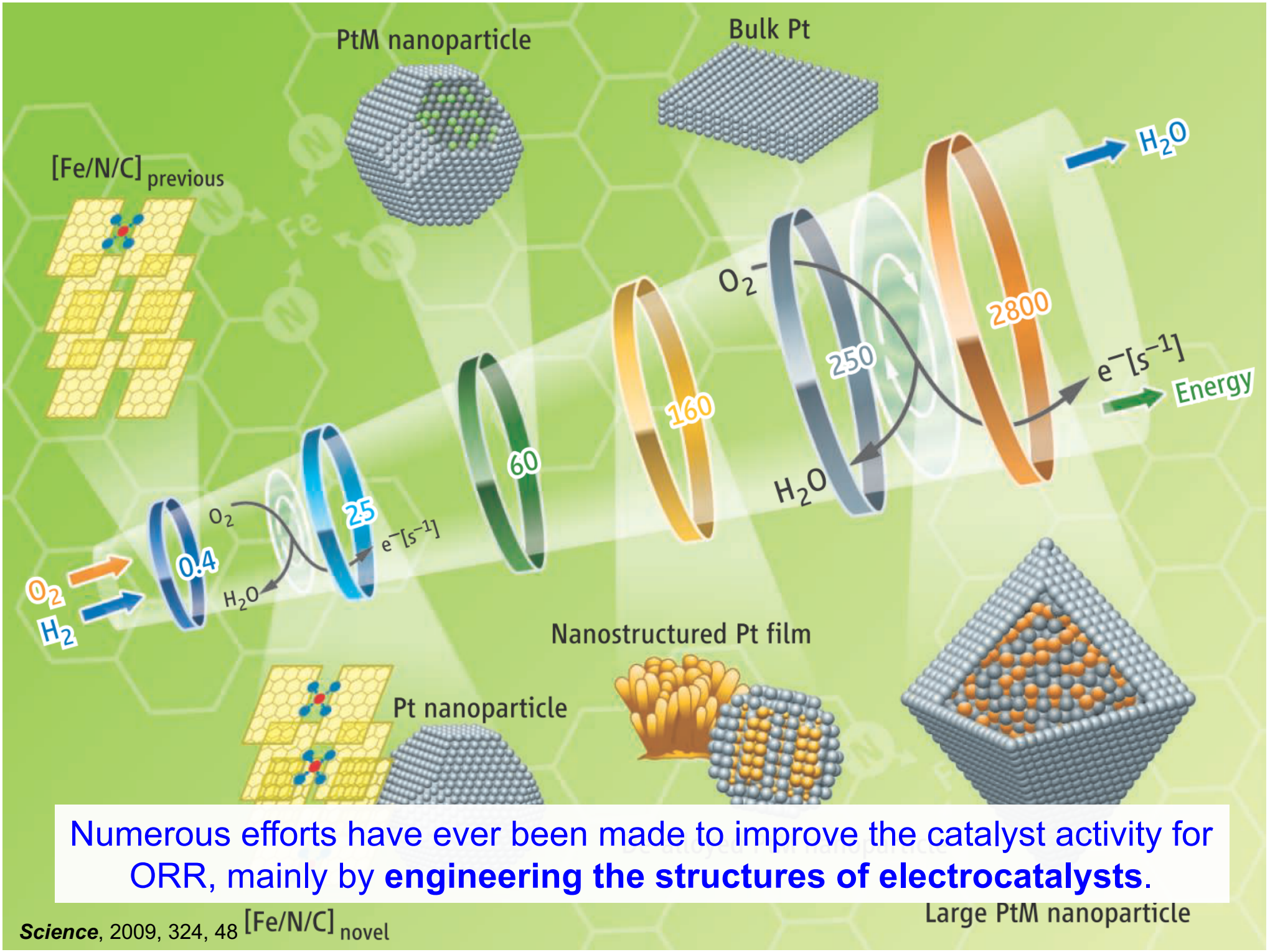
Japan: Toyota announced it will phase-out gasoline-powered cars entirely before **2050**.

Korea: The Ministry of Trade, Industry and Energy seeks to have more than 1 million eco-friendly cars on the road by **2020**.

The Netherlands, Norway, UK etc.: Pledged at COP21 talks to ensure all new vehicles are zero-emission models by **2050**.

China: Planning to switch the current subsidy-driven approach to zero-emission vehicle mandate.

Fuel Cell Technologies Market Report 2015, US DOE



Numerous efforts have ever been made to improve the catalyst activity for ORR, mainly by **engineering the structures of electrocatalysts**.

Science, 2009, 324, 48

New approach: Engineering the active site microenvironment with Ionic Liquids

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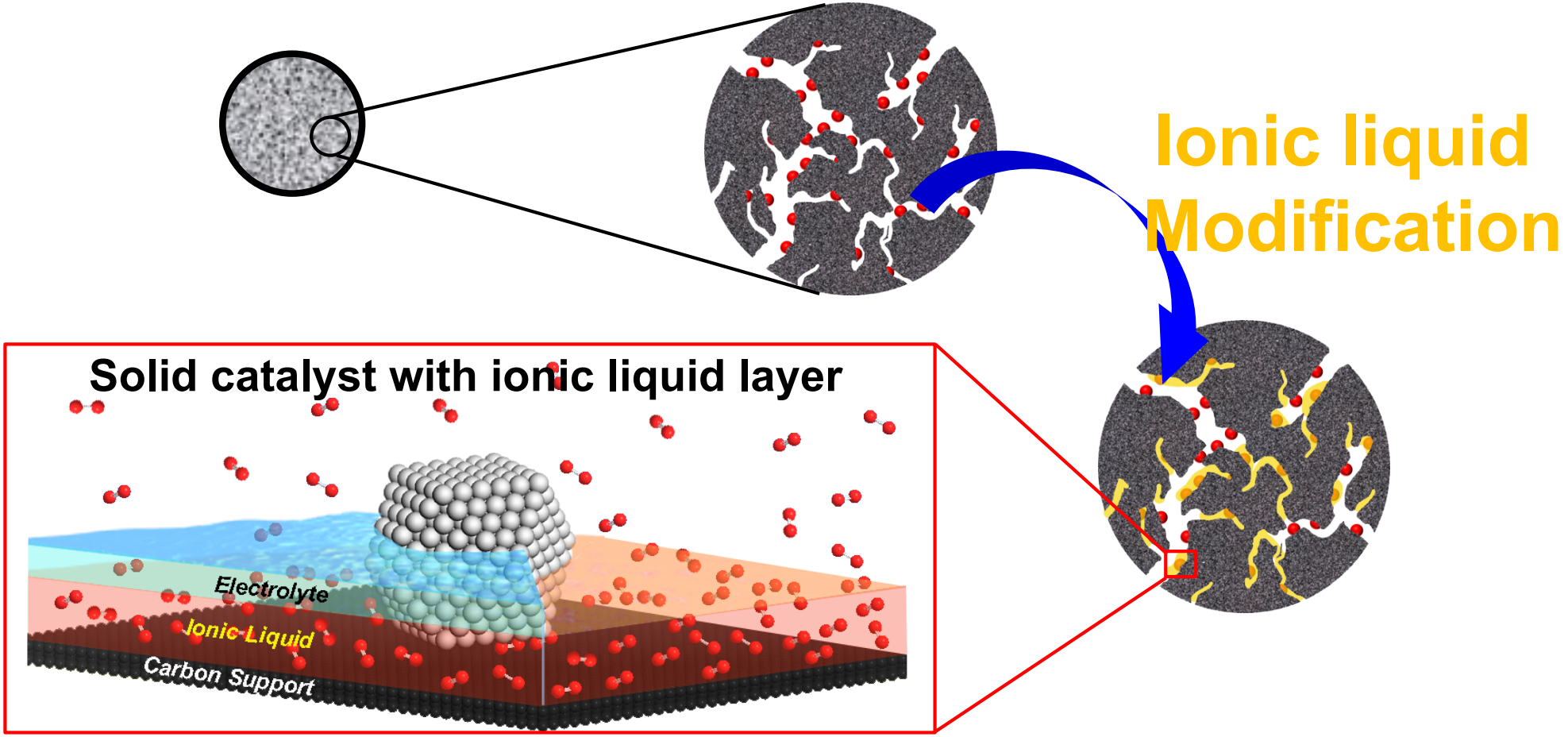

Kernchen et al. *Chem. Eng. Technol.* **30**, 985 (2007)
Zhang et al. *ACS Appl. Mater. Interfaces* ***18****, 3562-3570 (2015)*
Zhang et al. *Angew. Chem. Int. Ed.*, **55**, 2257-2261 (2016)

Materials

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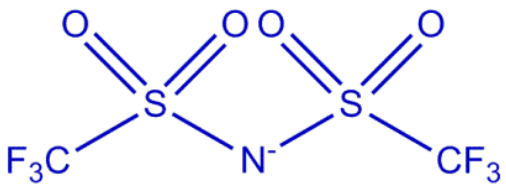
Catalyst: 20 wt.% Pt on carbon (Johnson Matthey HiSPEC)

Electrolyte: 0.1 M $HClO_4$

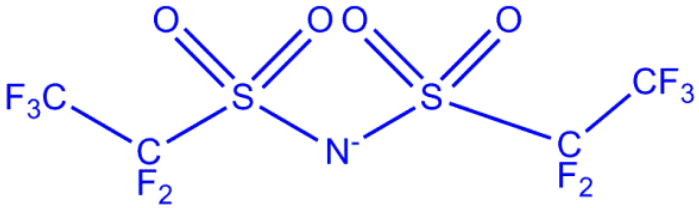
IL modification:

IL anions

[NTf2]$^-$

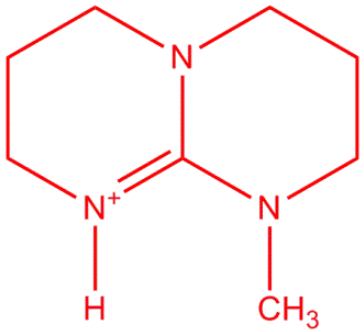


[Beti]$^-$

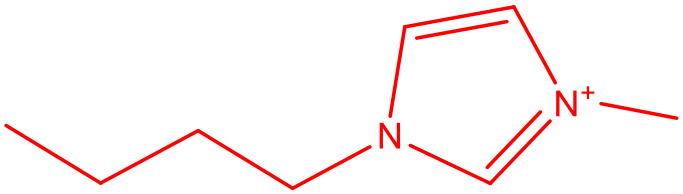


IL cations

[MTBD]



[C_4C_1Im]



ORR properties of IL modified Pt catalysts – *Effect of pore fillings*

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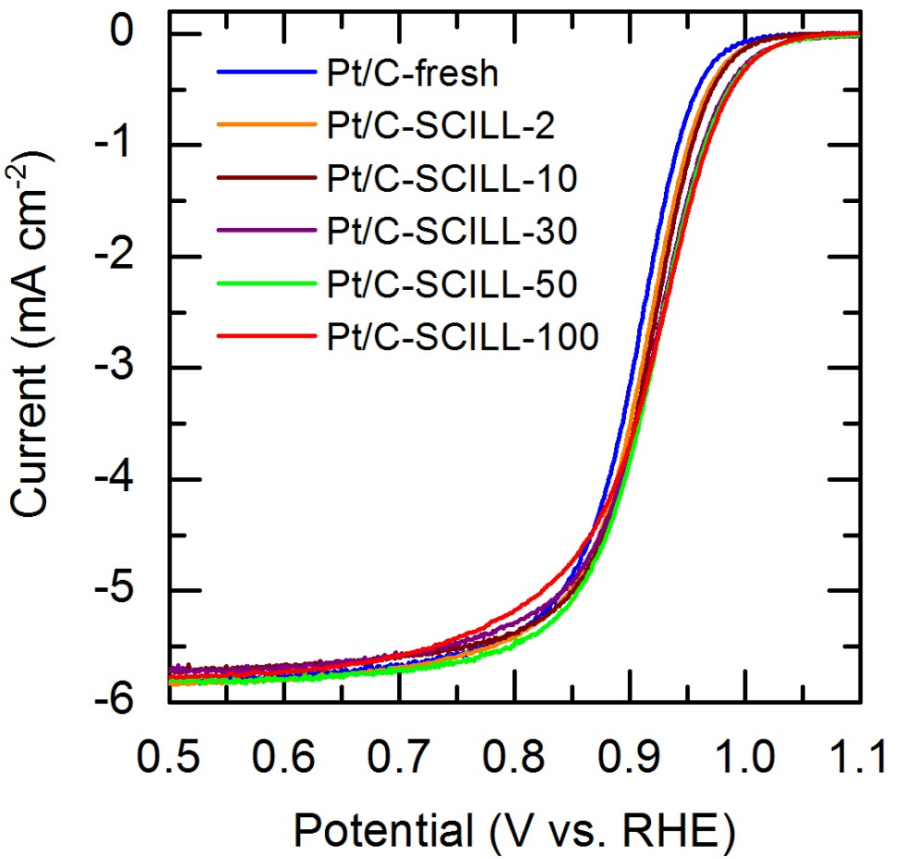

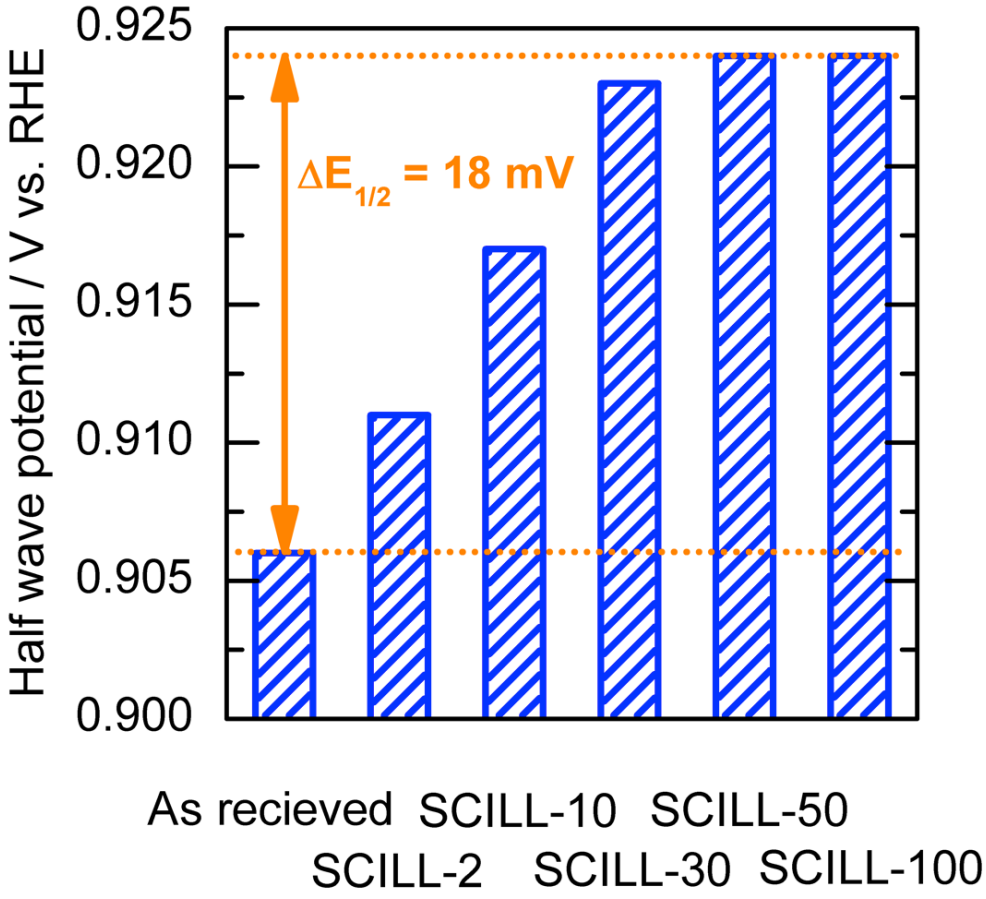

- Half wave potential shifts pronounced by 18 mV

0.1 M $HClO_4$, 10 mV s^{-1}, 1600 rpm, room temperature, [MTBD][NTf_2]

G.R. Zhang, M. Munoz, B.J.M. Etzold, *ACS Appl. Mater. Interfaces*, **2015**, *7*, 3562;
G.R. Zhang, B.J.M. Etzold, *J. Energy Chem.*, **2016**, *25*, 199.

ORR properties of IL modified Pt catalysts – *Effect of pore fillings*

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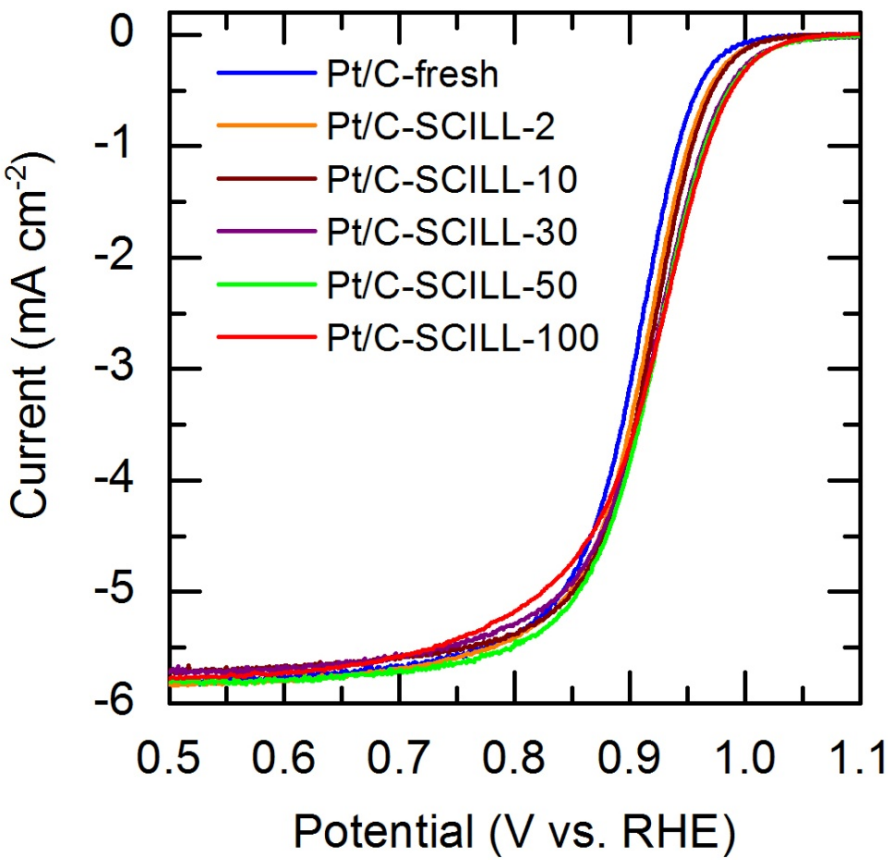

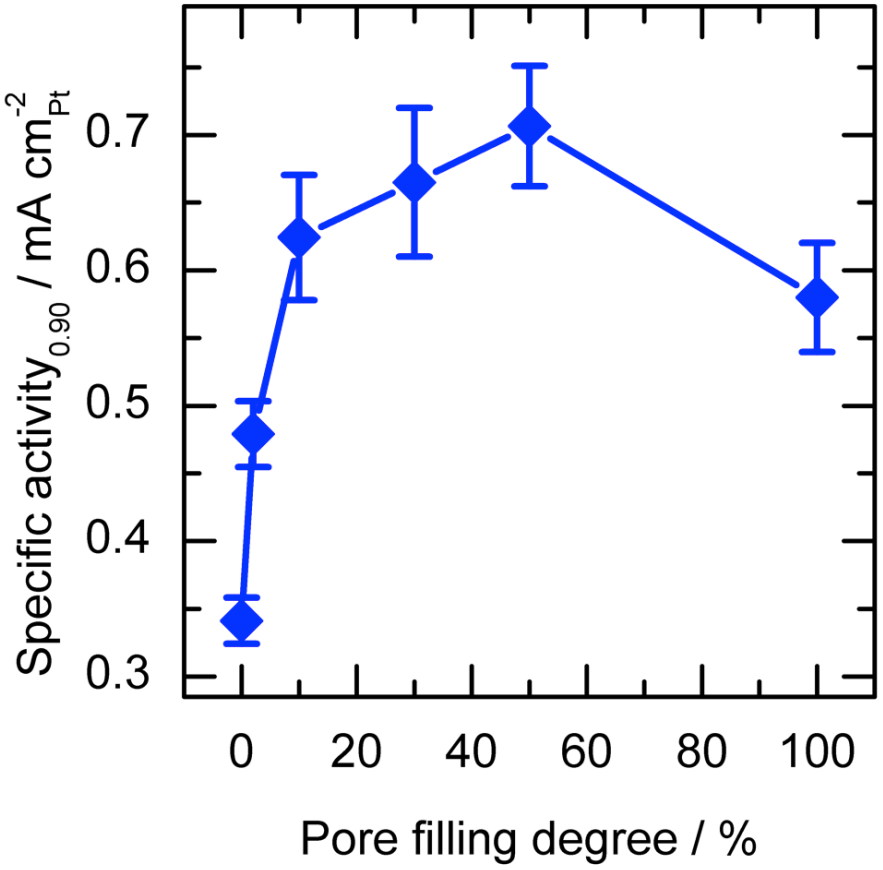

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ORR properties of IL modified Pt catalysts – *Effect of Anion Structures*

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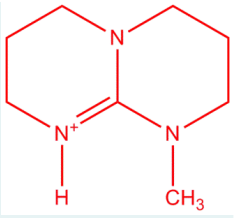
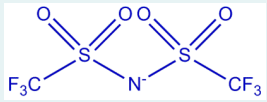
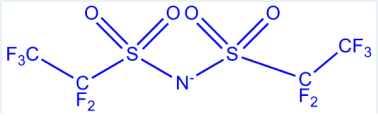
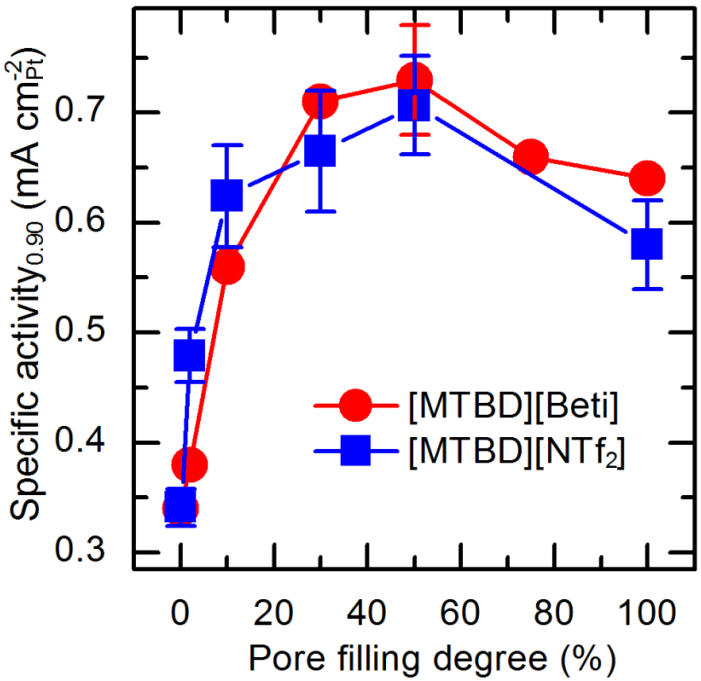
O_2 solubility matters?

	Cation	Anion	O_2 solubility (mM)
[MTBD][NTf_2]			2.2
[MTBD][Beti]			2.9



- Similar volcano dependent behaviour of Pt activity on pore filling, with the maximum activity obtained at α = 50%
- Pt activity towards ORR is not sensitive to the O_2 solubility in ILs.

ORR conditions: 0.1 M $HClO_4$, 10 mV s^{-1}, 1600 rpm, room temperature

ORR properties of IL modified Pt catalysts – *Effect of Cation Structures*

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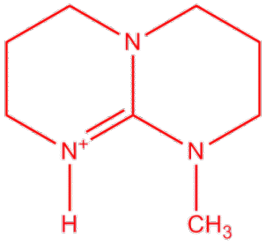
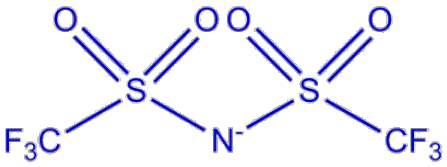
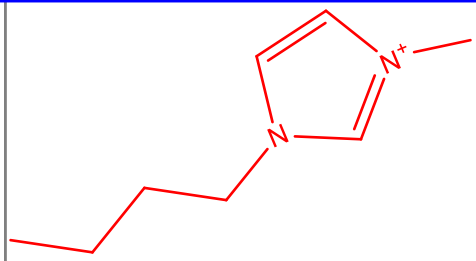
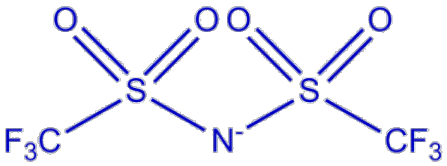
	Cation	Anion	O_2 solubility (mM)
$[MTBD][NTf_2]$			2.2

	Cation	Anion	O_2 solubility (mM)
$[C_4C_1im][NTf_2]$			2.3

G.R. Zhang et al. *Angew. Chem. Int. Ed.* **55**, 2257 (2016)

ORR properties of IL modified Pt catalysts – *Effect of Cation Structures*

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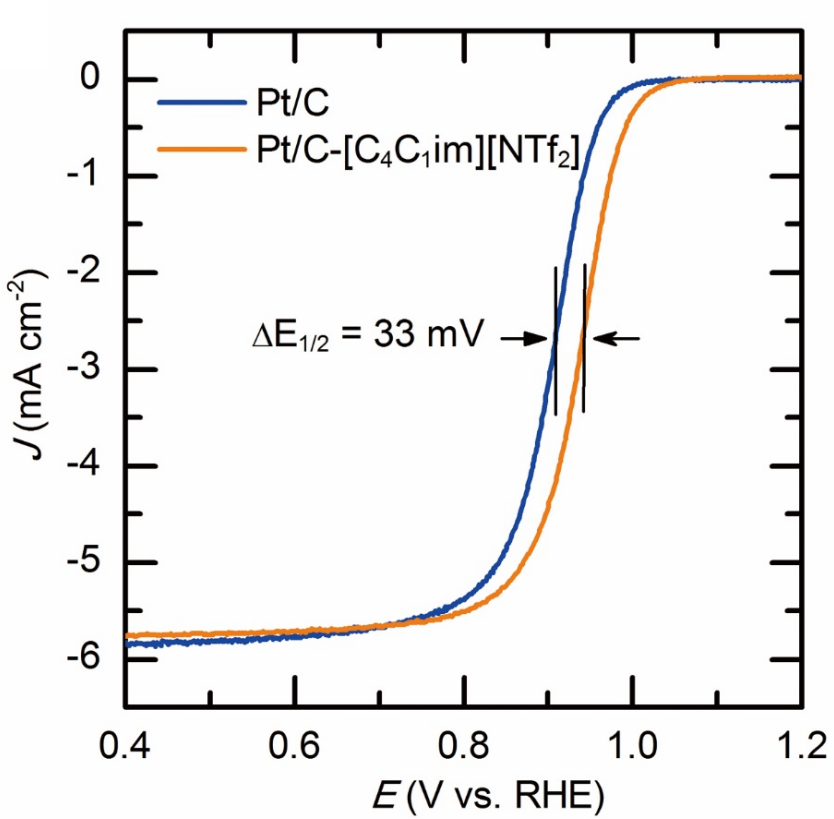
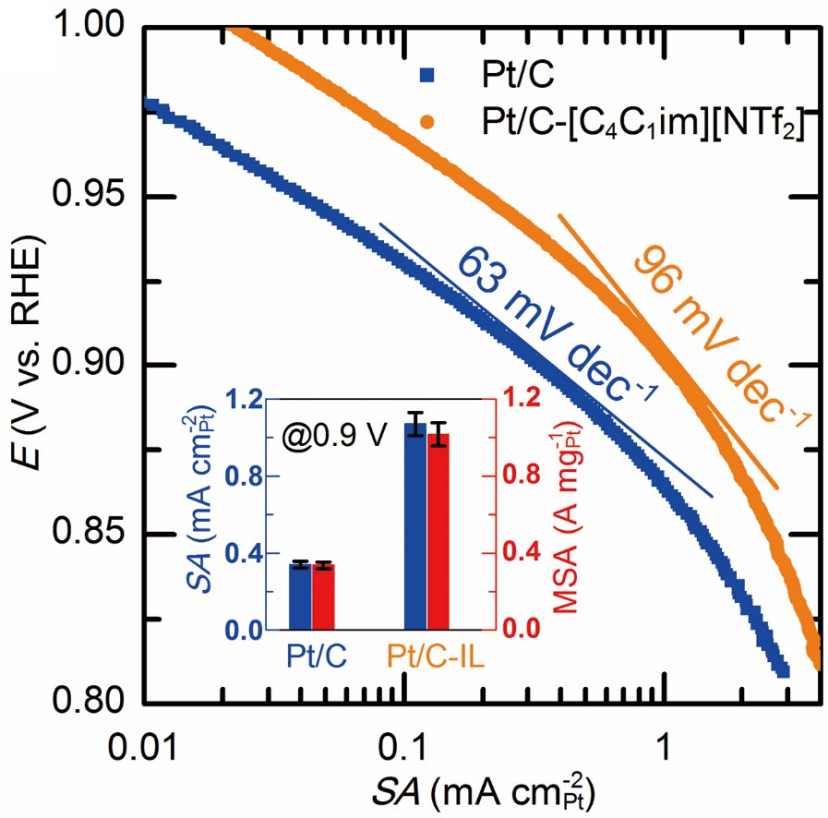
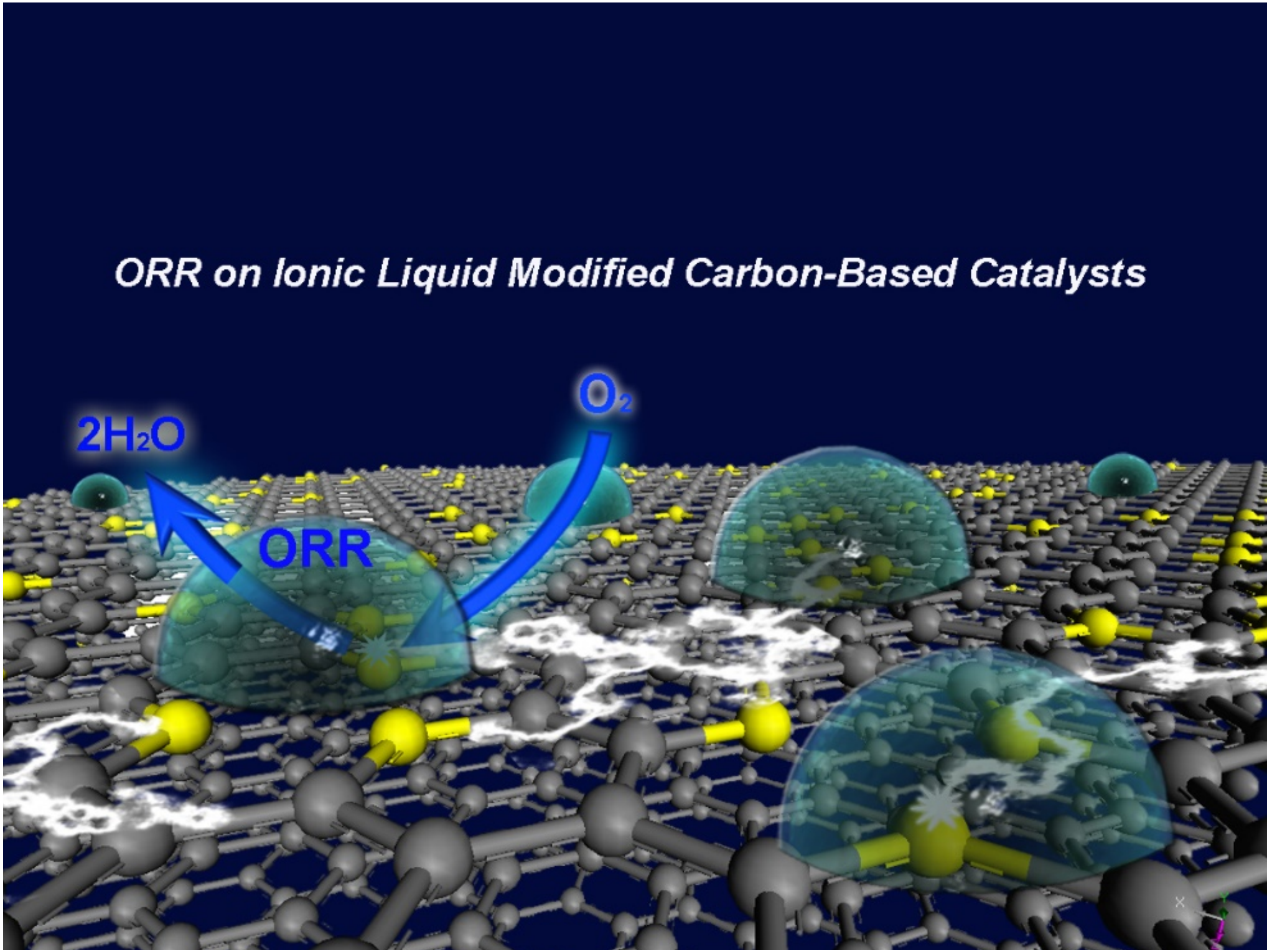




- Pt/C-[C_4C_1im][NTf_2] exhibited the highest activity towards ORR, which is three times more active than the pristine Pt/C

0.1 M $HClO_4$, 10 mV s^{-1}, 1600 rpm, room temperature, [C_4C_1im][NTf_2]

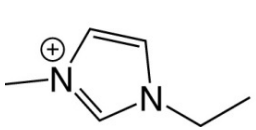
G.R. Zhang et al. *Angew. Chem. Int. Ed.* **55**, 2257 (2016)

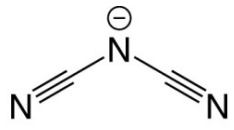

ORR on Ionic Liquid Modified Carbon-Based Catalysts
O2
2H2O
ORR

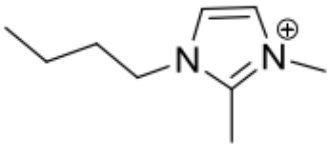
Synthesis procedure

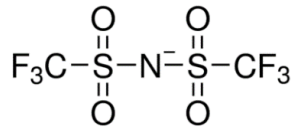
Carbon support (Ketjenblack)

1. Impregnating with nitrogen source ([EMIM][dca])







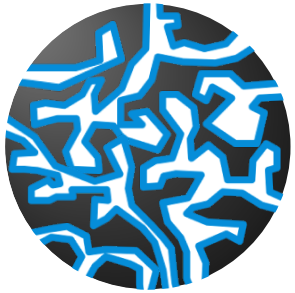


3. IL modification with [BMMIM][NTf2]

- The synthesis was done according to a recipe described in literature [4]

2. Thermal decomposition at 900 °C under nitrogen atmosphere

N-Doped Carbon



SCILL Catalyst

N. R. Sahraie, et al. *J Am Chem Soc* **2014,** *136(41)*, 14486-14497.

IL Modification of N-doped Carbon

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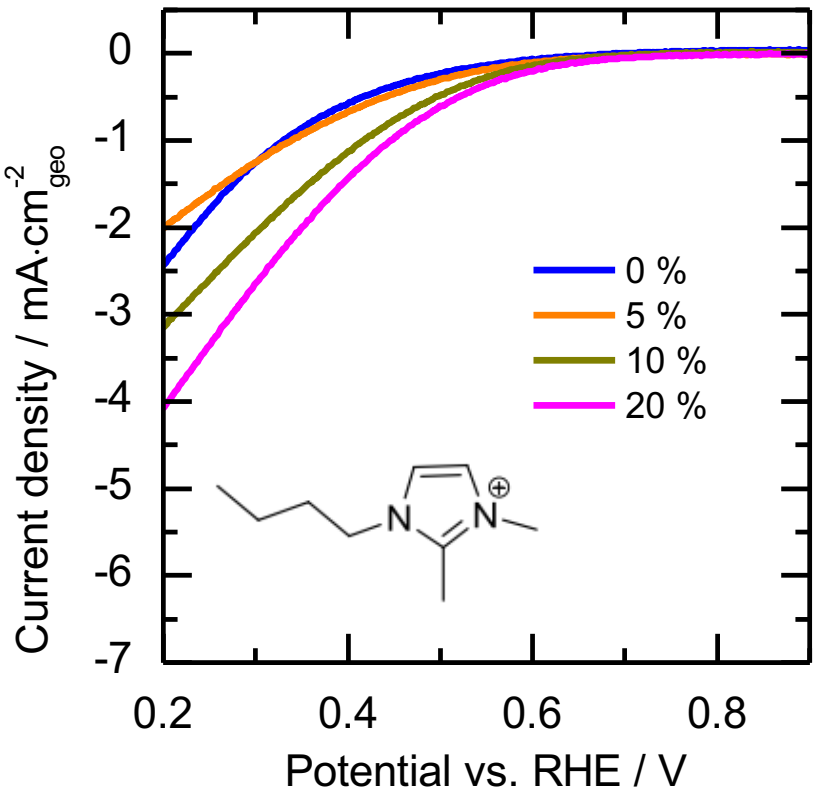
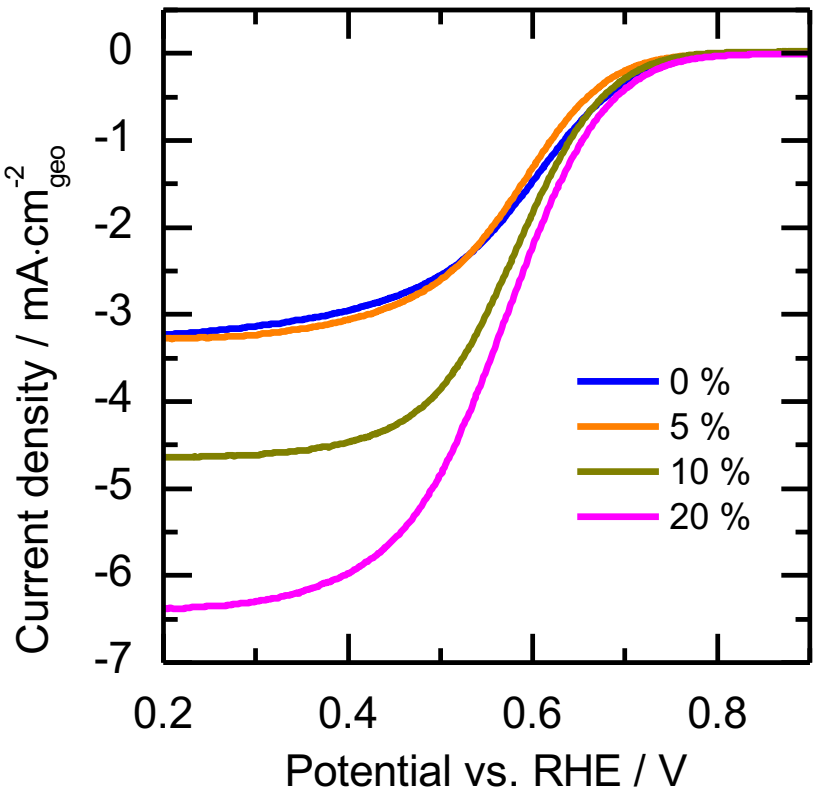
- ORR polarization curve in **acidic** electrolyte (**$HClO_4$**, 1600 rpm, 0.92 mg/cm²)



- ORR polarization curve in **alkaline** electrolyte (**KOH**, 1600 rpm, 0.92 mg/cm²)



- [BMMIM][NTf_2] can boost the activity of N-Doped carbon in acidic and alkaline media

IL Modification of N-doped Carbon

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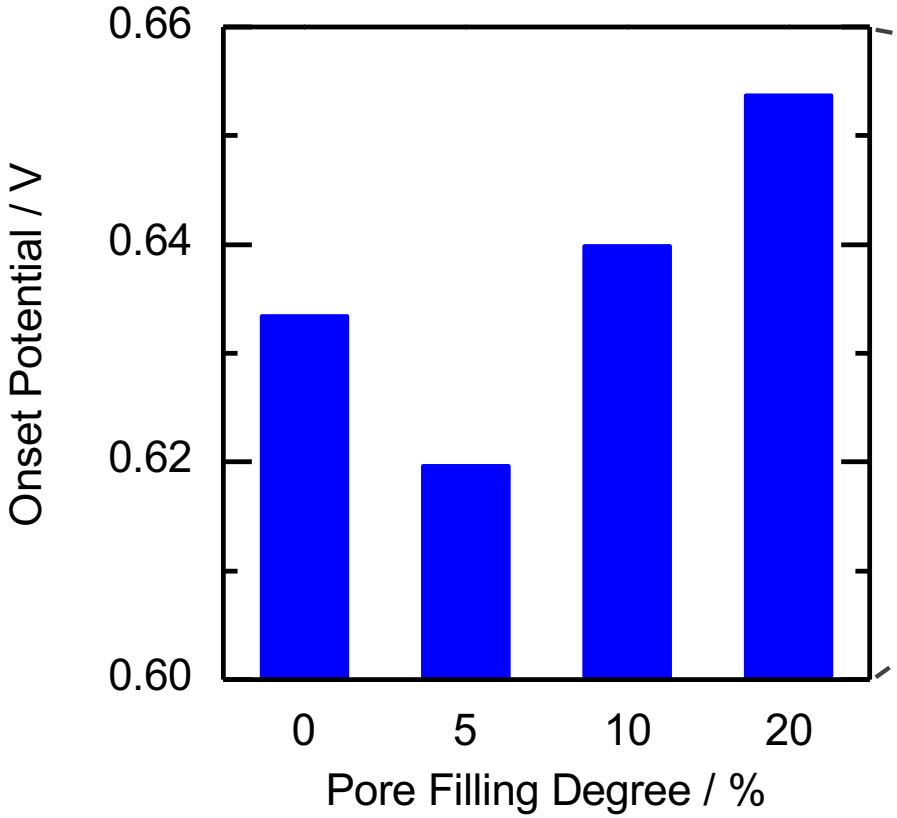
- Onset Potential



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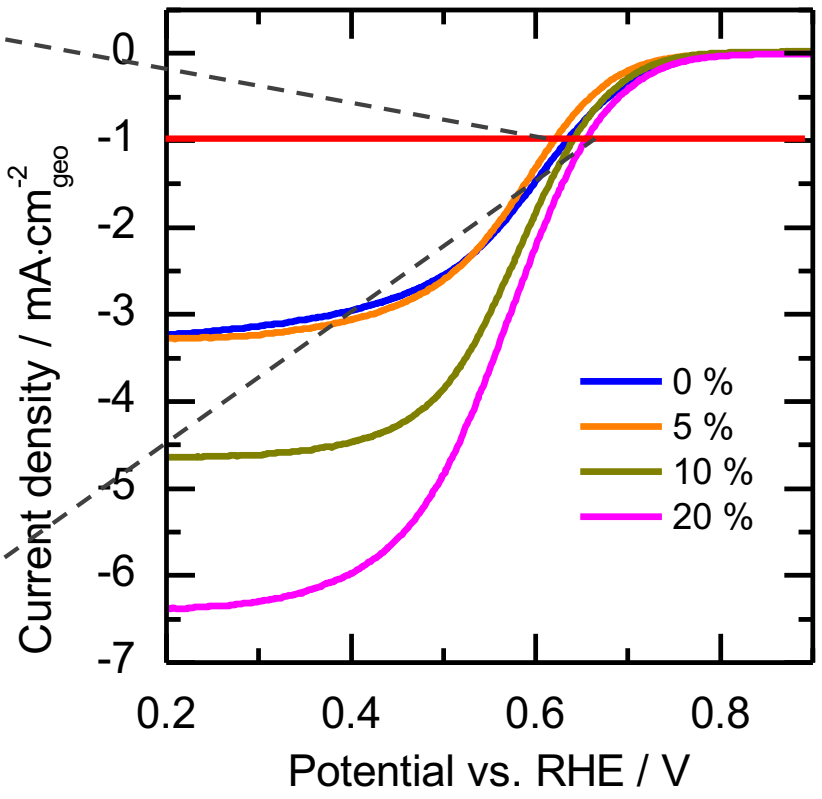

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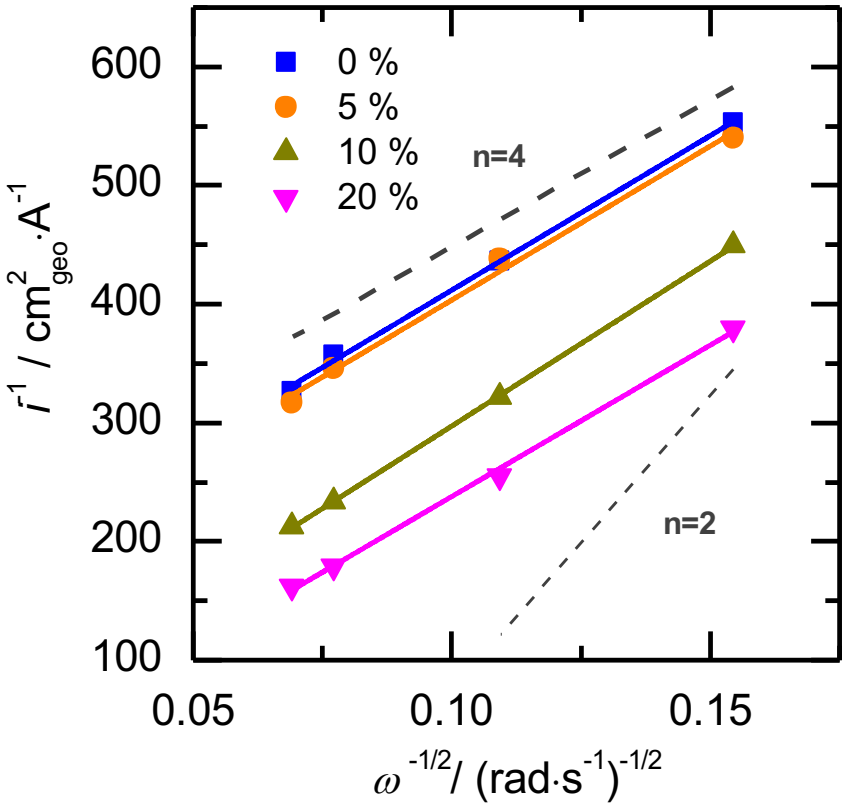
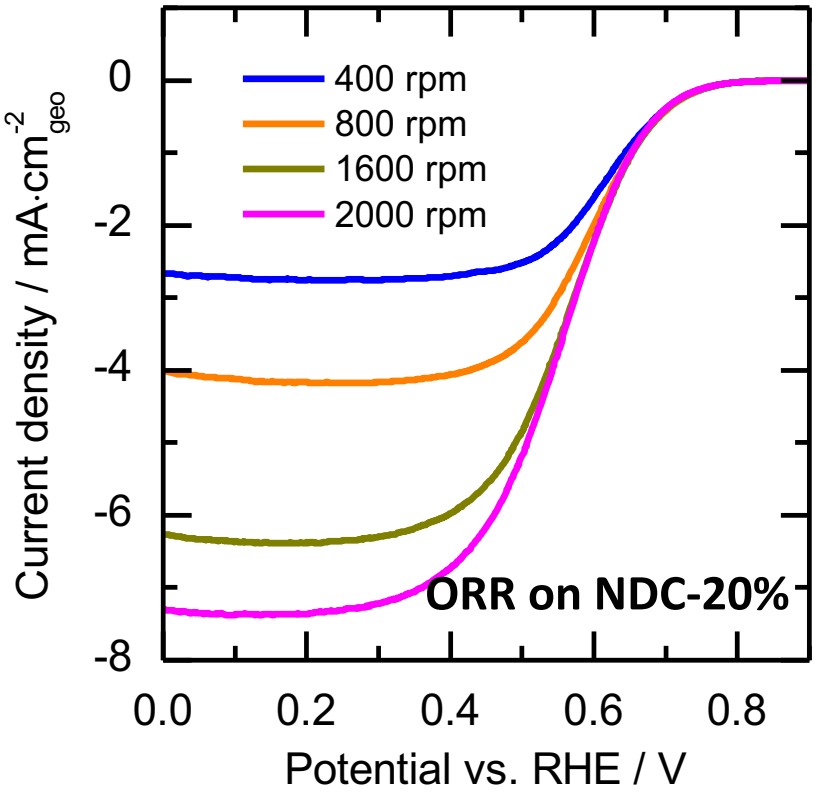
Koutecky-Levich Analysis

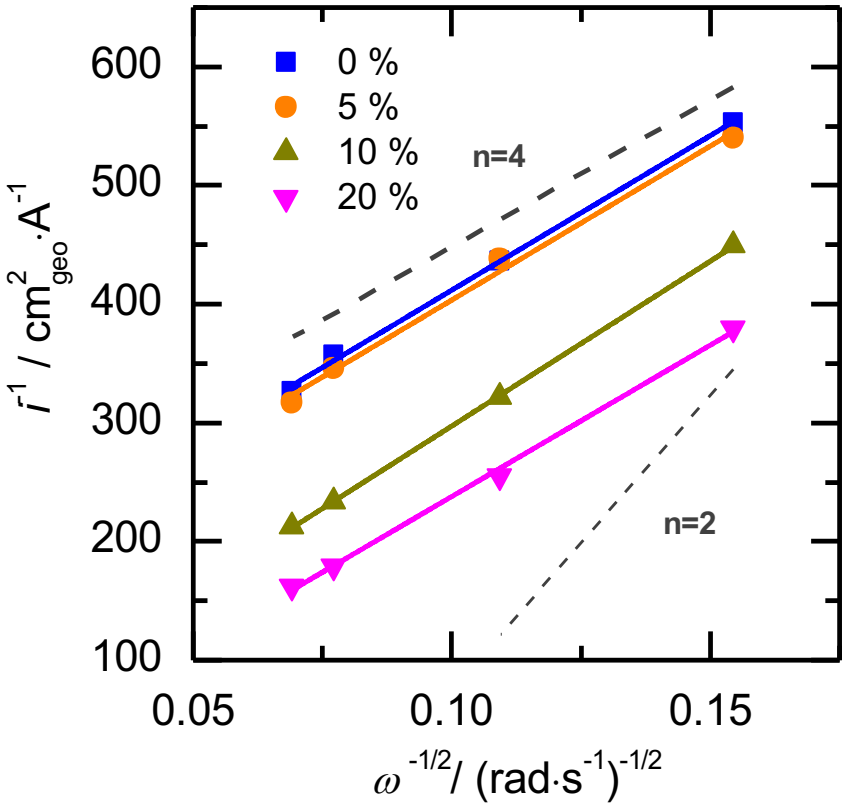


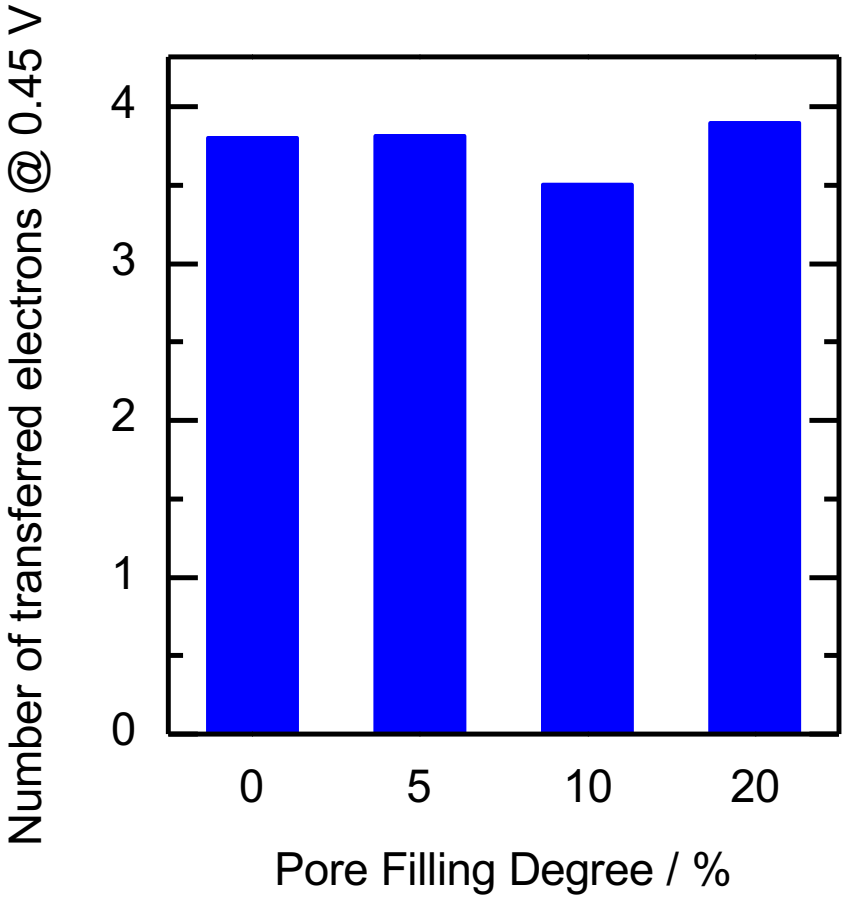


Koutecky-Levich Equation:

$$-\frac{1}{I} = -\frac{1}{I_k} + \frac{1}{0.62nFAD^{2/3}\nu^{-1/6}\omega^{1/2}C_{O_2}}$$

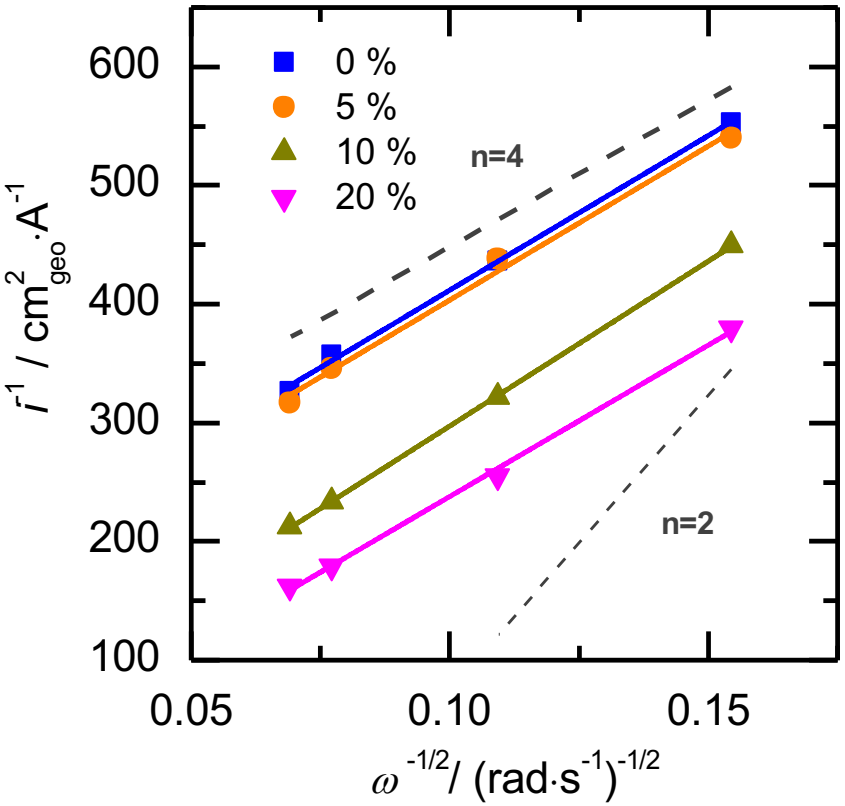
Koutecky-Levich Analysis -Electron transfer number *n*

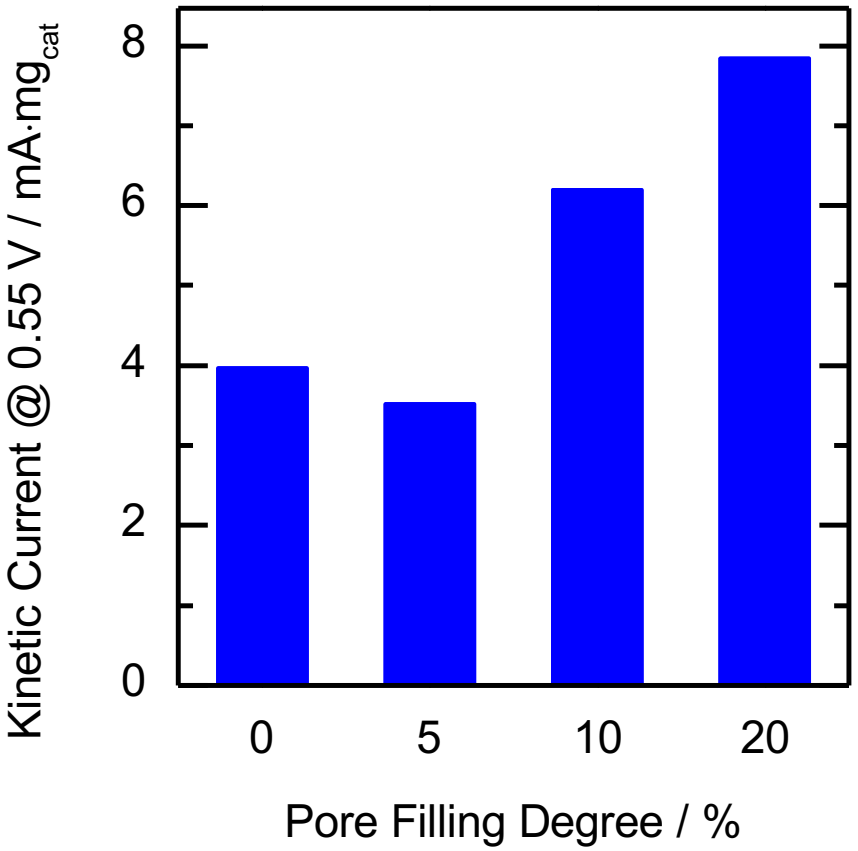




- The selectivity is not influenced by the IL modification

Koutecky-Levich Analysis -Kinetic current I_k





- The activity can be boosted for up to two times after IL modification

Stability of IL-modified NDC

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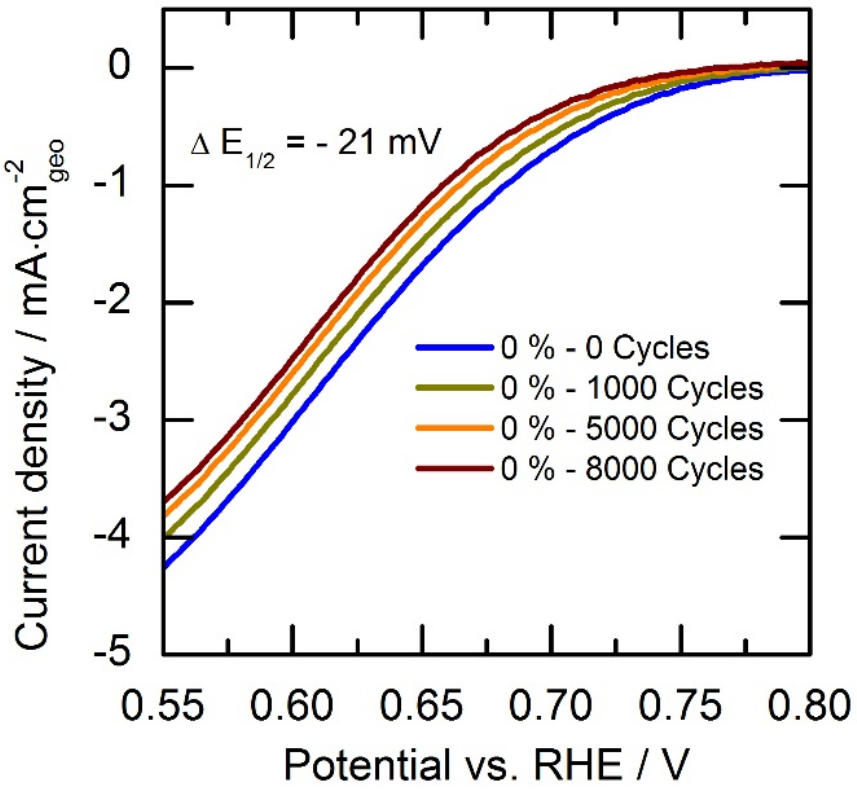
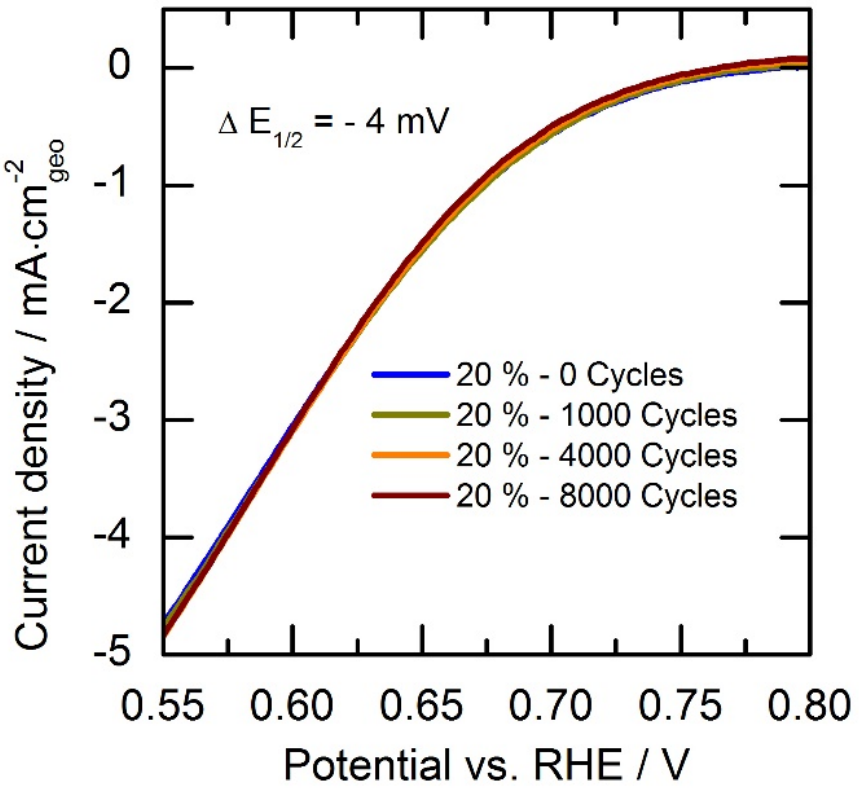
NDC-0%



NDC-20%



Repeated potential cycling between 0.6 to 1.4 V in O_2-saturated 0.1 M KOH electrolyte

- IL-modified NDC exhibit superior stability for ORR

Manuscript in preparation

Summary

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- **The introduction of IL could significantly improve the catalytic activity of Pt/C and NDC for ORR.**
- **The boosting effect is dependent on the pore filling and geometric structures of ILs.**
- **The boosting effect could be stabilized after the accelerated durability test.**
- **SCILL concept: a new strategy to improve the performance of electrocatalysts for fuel cells.**

O_2 solubility

Acknowledgement

European Research Council
Established by the European Commission

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Thank you for your attention