芳香族高分子の合成・機能化と触媒材料への展開 ①

Tokyo Tech

難波江裕太（なばえゆうた）

ロケーション
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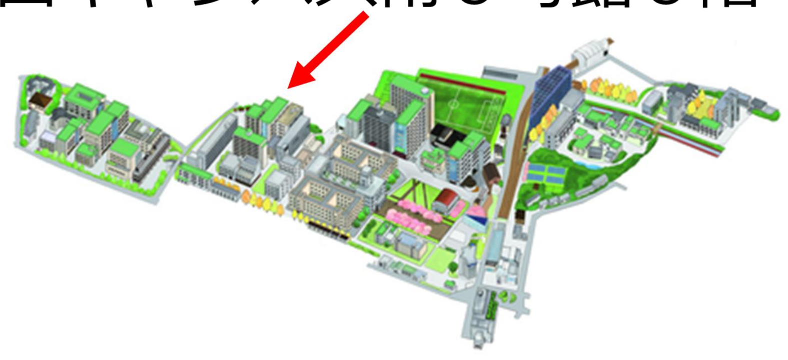
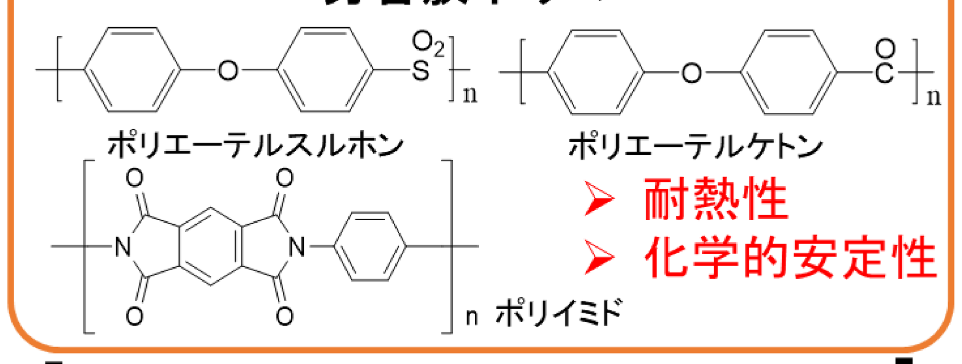
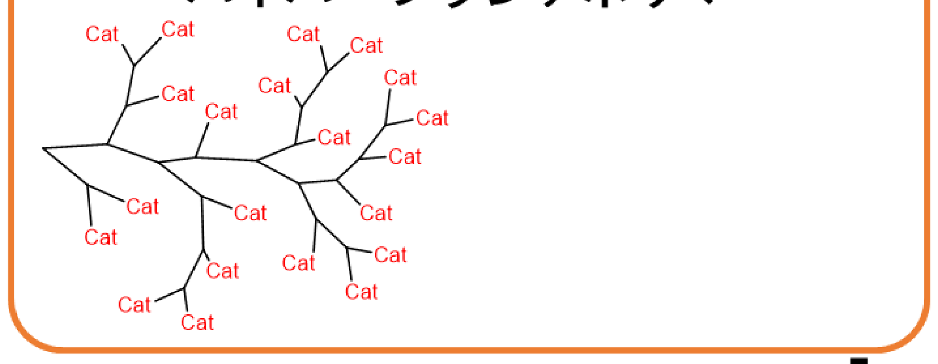


所属：物質理工学院材料系
専門：触媒化学，電気化学，高分子化学

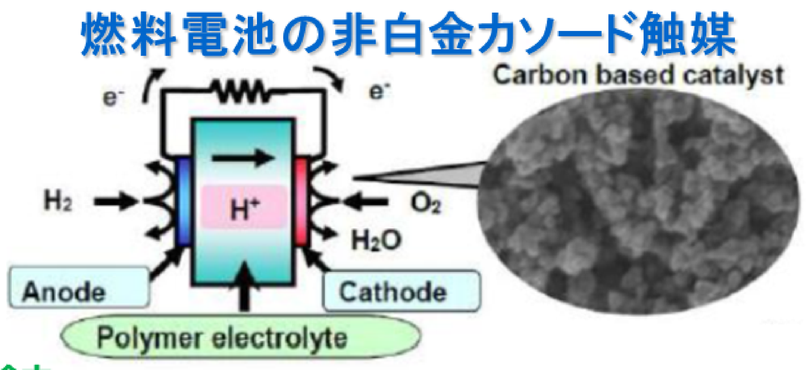




熱処理による炭素化
ポリイミドの不融性を活かした粒子形態の制御

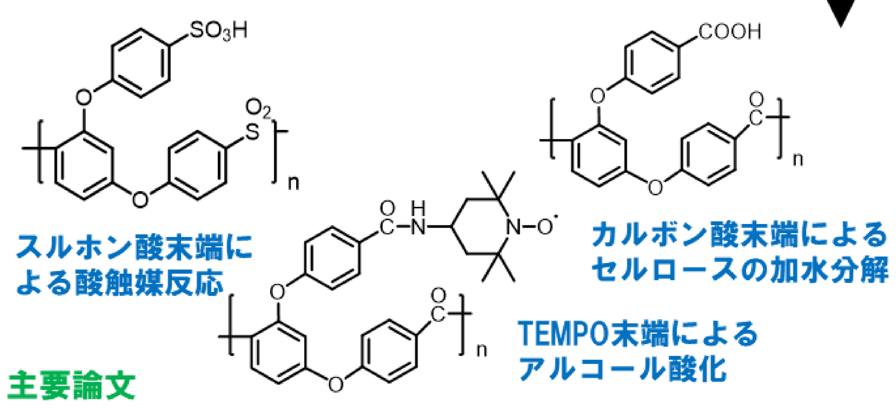
末端を活性点とした触媒材料開発

燃料電池の非白金カソード触媒



主要論文
- Nabae et al, *J. Mater. Chem A* (2014) 2, 11561.
- Nabae et al, *Sci. Rep.* (2016) 6, 23276.
- Muthukrishnan et al., *J. Phys. Chem. C* (2016) 120, 22515.

外部資金
- NEDO 固体高分子形燃料電池利用高度化技術開発 NEDO
- 共同研究（複数社）



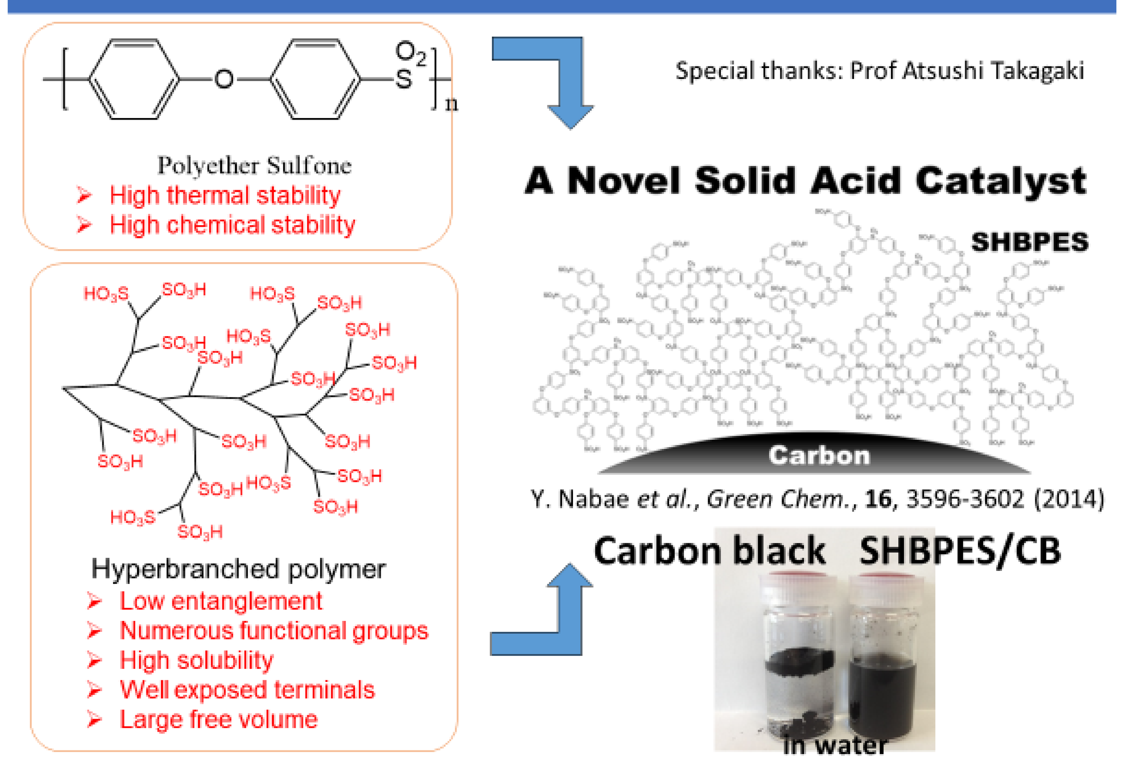
主要論文
- Nabae et al, *Green Chem.* (2014) 16, 3596.
- Shi et al, *RSC Adv..* (2015) 5, 1923.
- Nabae et al, *Polymer* (2018) 137, 324.

外部資金
- 科研費若手B 科研費 KAKENHI

ポリイミドやポリエーテルスルホンなどの芳香族高分子は、耐熱性や化学的安定性に優れていますが、触媒の分野での活用はこれまで多くありません。私は芳香族高分子の持つ普遍的な特長が、触媒材料やその前駆体として好適であると考え、①芳香族ハイパーブランチポリマーの末端を触媒活性点とした、新規触媒材料の開発、②ポリイミド微粒子の炭素化によって得た炭素粉末の燃料電池触媒への展開、などのテーマを実施しています。

研究紹介１：芳香族ハイパーブランチポリマーの合成と触媒反応

芳香族ハイパーブランチポリマーと固体酸触媒



Y. Nabae *et al.*, *Green Chem.*, **16**, 3596-3602 (2014)

Synthesis of HBSPES/CB

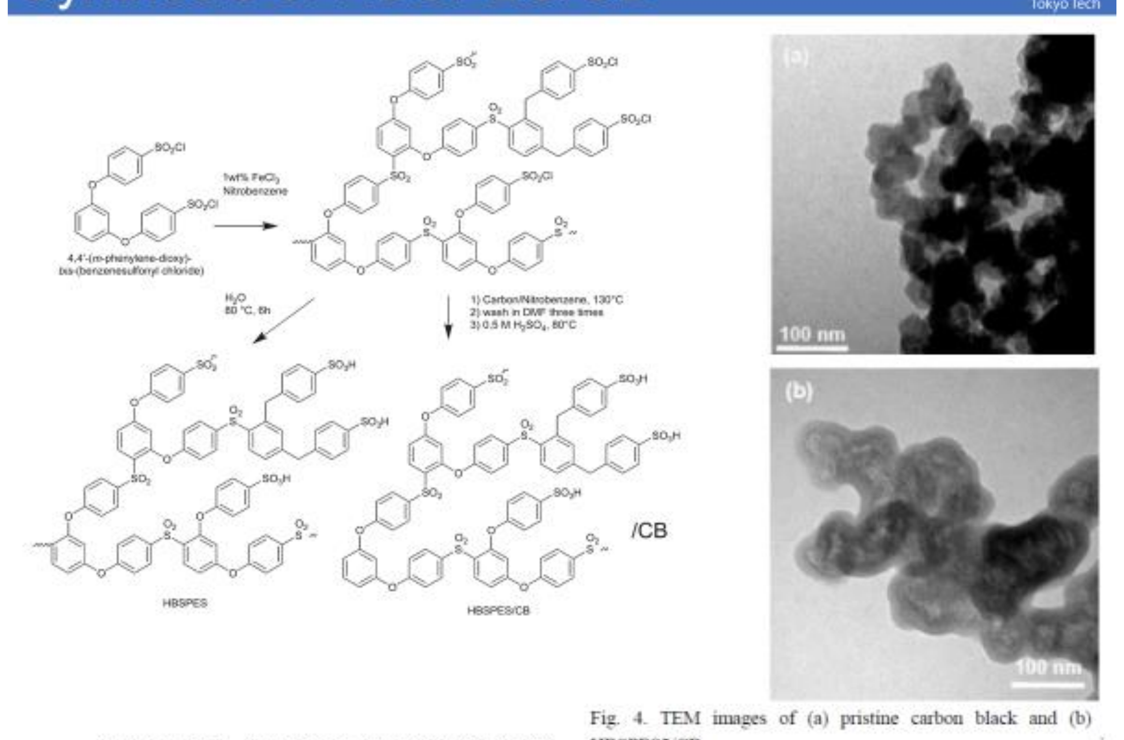
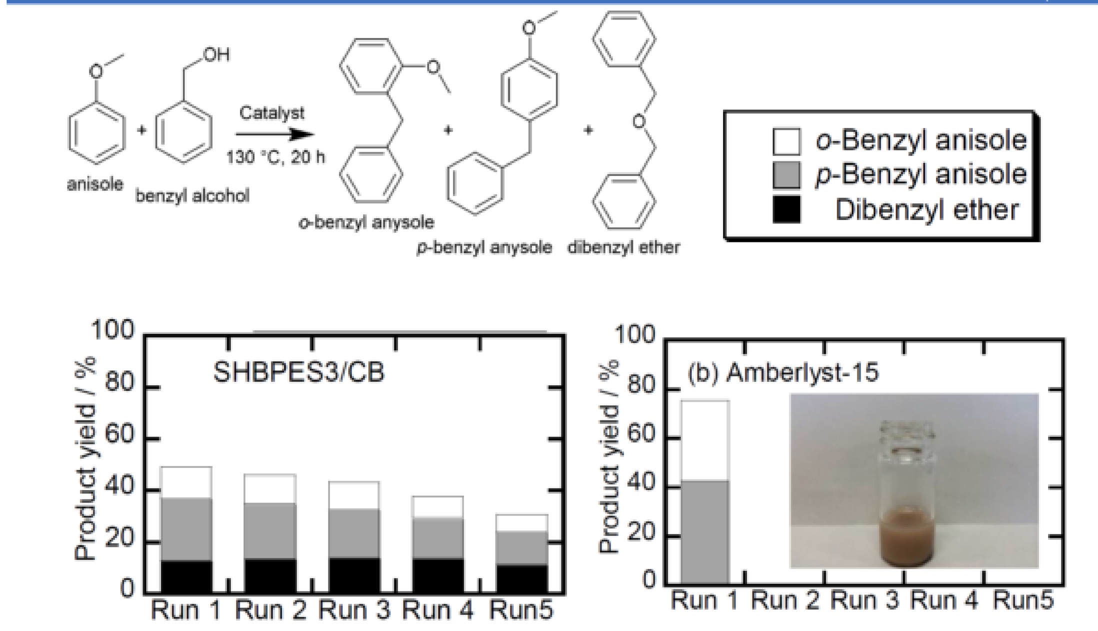


Fig. 4. TEM images of (a) pristine carbon black and (b) HBSPES3/CB.

Y. Nabae *et al.*, *Green Chem.*, **16**, 3596-3602 (2014)

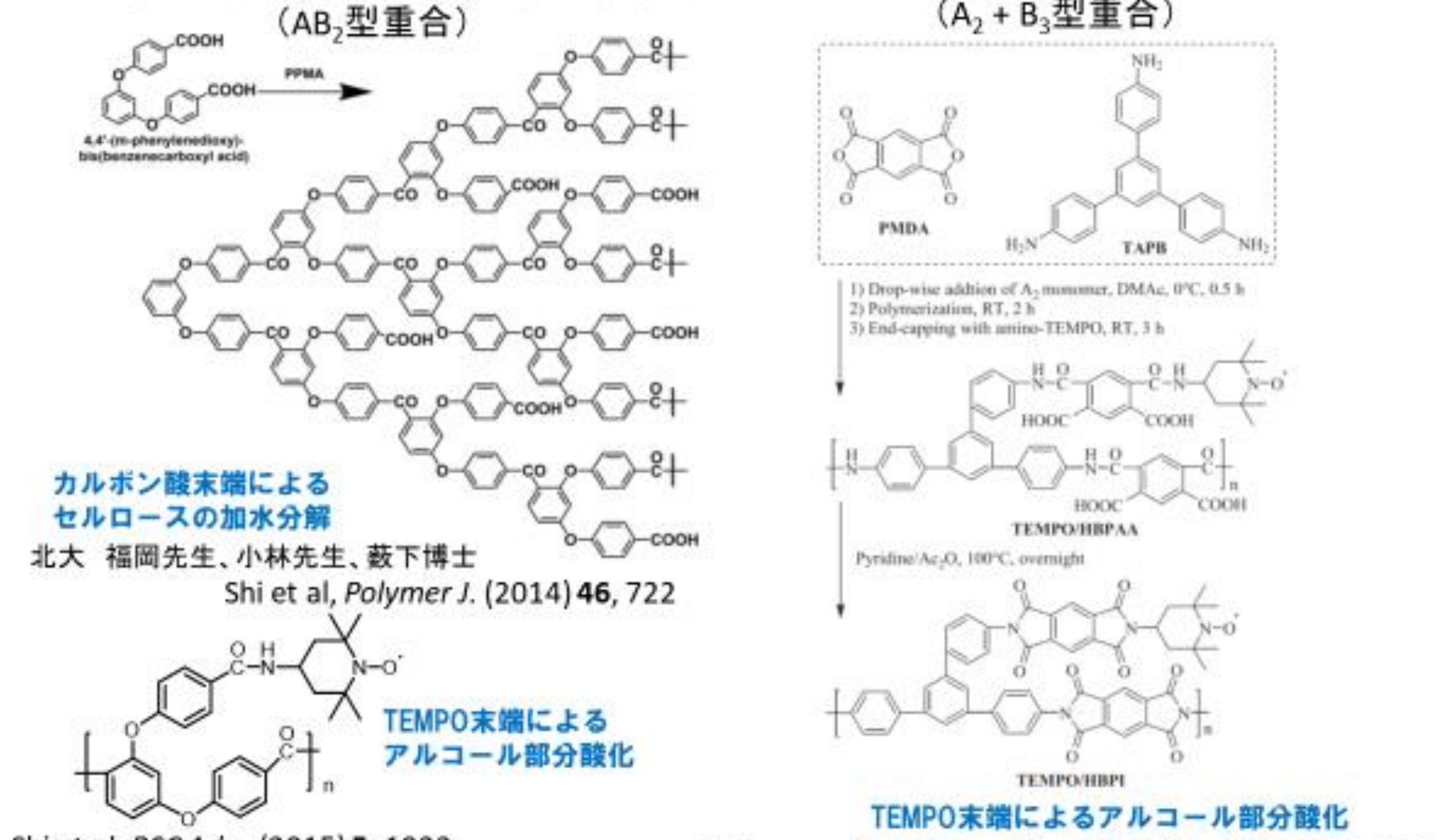
高温での反応の例



Much better stability than amberlyst-15

Y. Nabae *et al.*, *Green Chem.*, **16**, 3596-3602 (2014).

多様な触媒活性点への展開

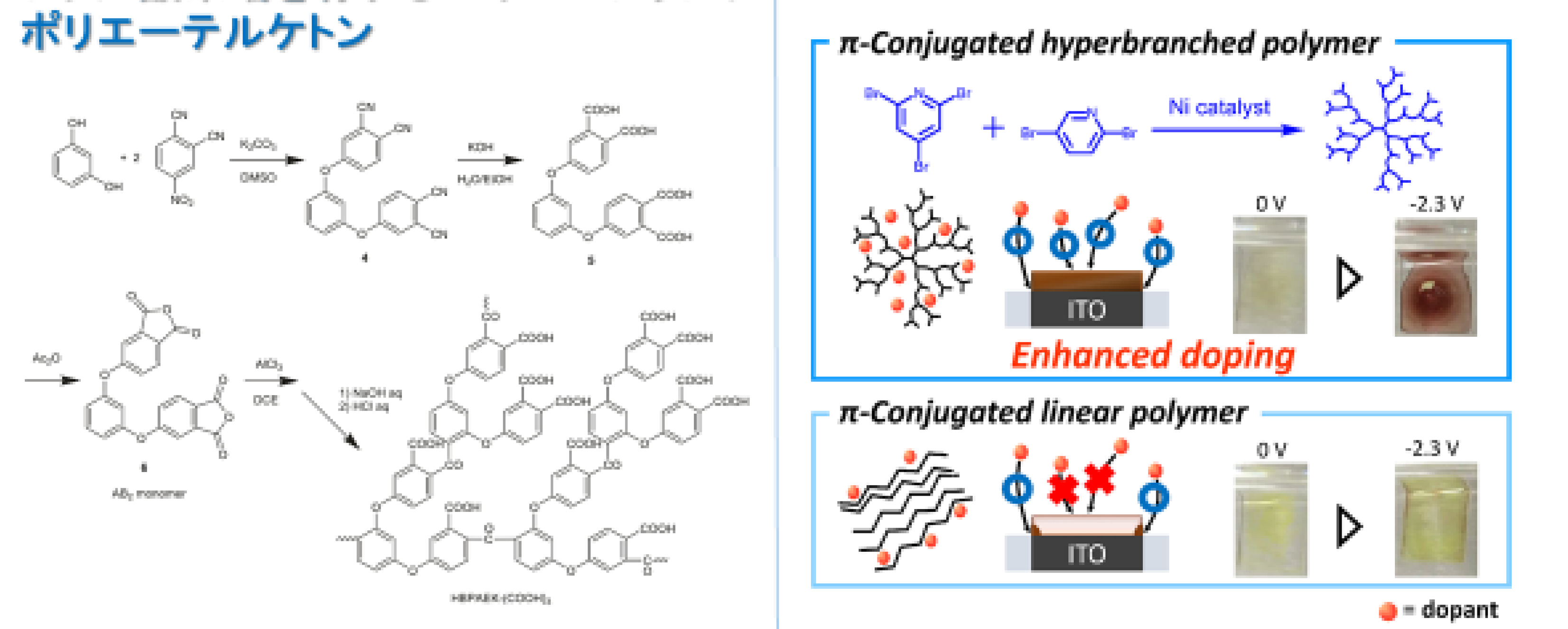


北大 福岡先生、小林先生、薮下博士
Shi et al, *Polymer J.* (2014) **46**, 722

Shi et al, *RSC Adv..* (2015) **5**, 1923.
Shi et al, *J. Photopolym. Sci. Technol.* (2015) 28, 187.

Nabae et al., *J. Photopolym. Sci. Technol.* (2014) **27** 139.
Nabae et al, *High Perform. Polym.* (2017) **29** 646.

最近研究しているポリマー



Nabae *et al*, *Polymer J.*, published online (2018).
12月号 Highlight!

Koga *et al*, *Macromol. Chem. Phys.* **2017**, 1700391.
Koga *et al*, *J. Photopolym. Sci. Technol.*, **31**, 617 (2018).
Special thanks: Dr Akiyasu Funakawa (Asahi KASEI)

今後様々な触媒反応へ・・・

本研究は科研費を利用して実施しています。科研費 KAKENHI

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芳香族高分子の合成・機能化と触媒材料への展開　②

Tokyo Tech

研究紹介２：含窒素ポリマーの炭素化と燃料電池触媒への展開

Proton Exchange Membrane Fuel Cells (PEMFCs)

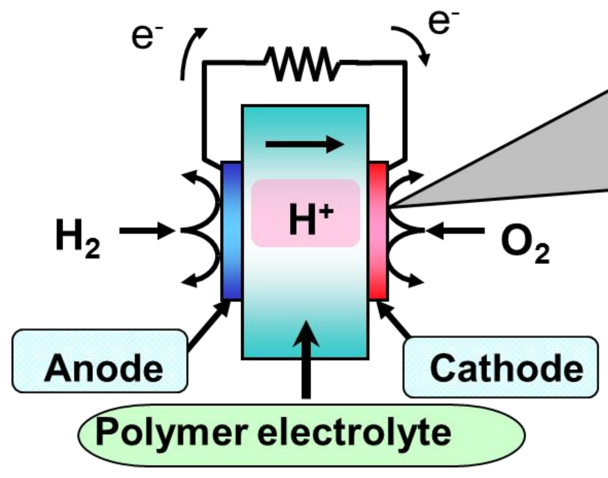
Directly convert the chemical energy from a fuel into electricity

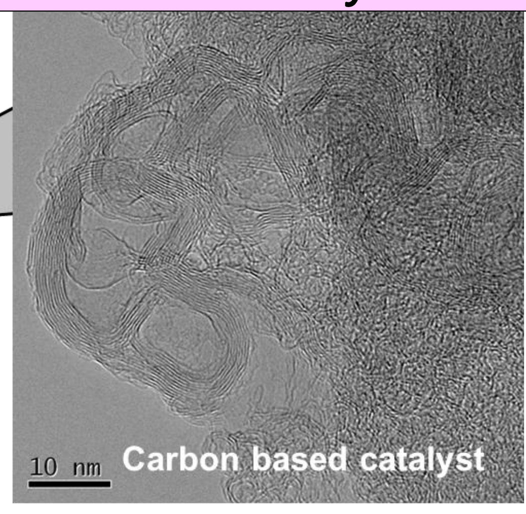
High conversion efficiency!
High energy density!

Application in automobiles!?

TOYOTA MIRAI
US$57,400

Carbon-Based Catalyst

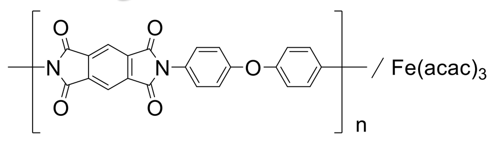




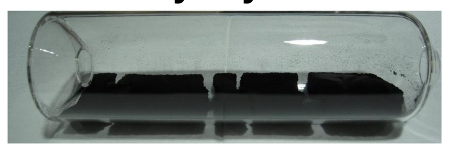
Pt catalyst is necessary to achieve a high enough reaction rate.
Especially cathode reaction is slow → High loading of Pt

Non-Precious-Metal Catalyst is desired.

Our Material Synthesis



Pyrolysis : under N_2 or NH_3 flow, 600-1000˚C



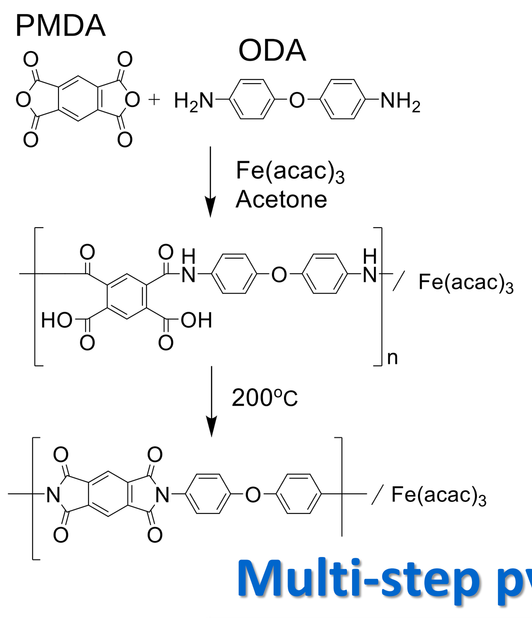
Ball mill, AW

Synthesis of new carbon materials rather than surface modification

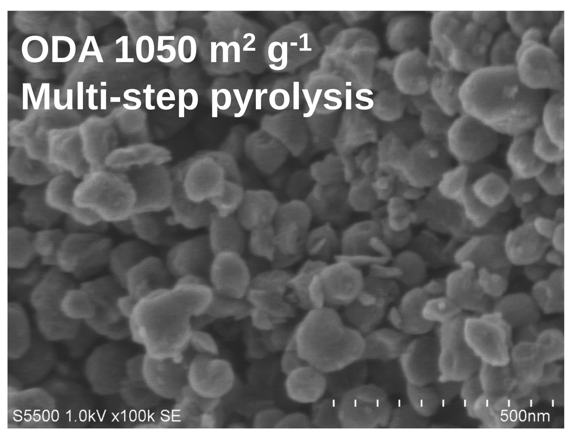
Many active centers?
High durability?

・Y. Nabae et al, *Catal. Sci. Technol.* 2014, **4**, 1400.
・Y. Nabae et al, *J. Mater. Chem. A.* 2014, **2**, 11561

Synthesis and Characterization



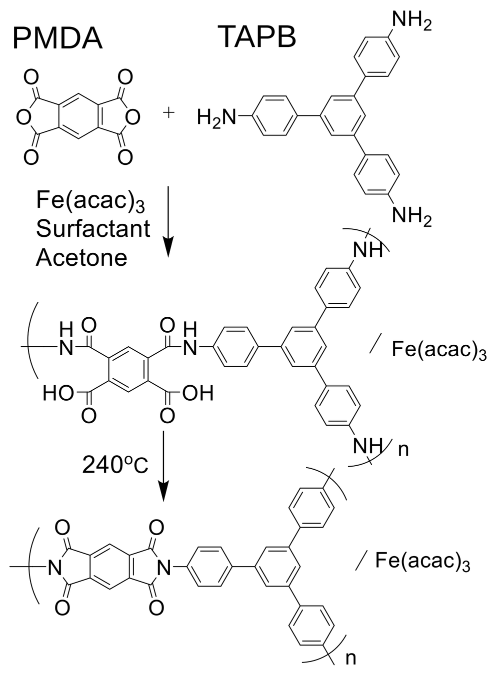
FE-SEM

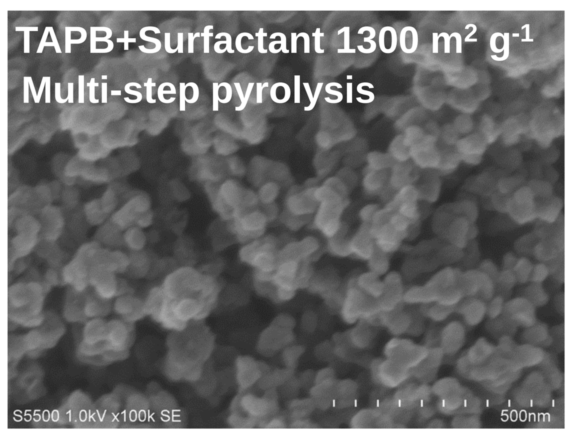


C: 90.6%, H: trace, N: 3.1%, Fe: 1.9%, BET: 1050 $m^2\ g^{-1}$

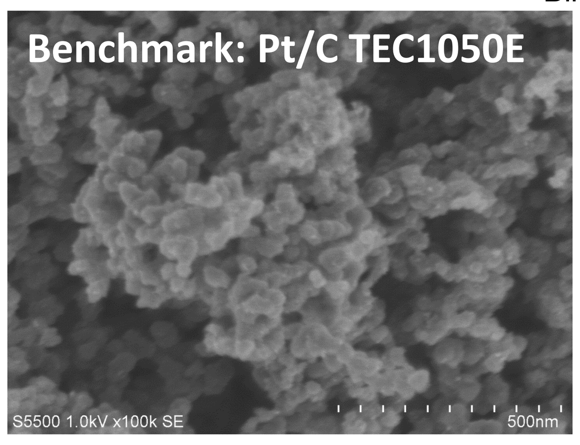
Multi-step pyrolysis

600ºC (N_2) ⇨ AW Ball mill ⇨ 800ºC (NH_3) ⇨ AW ⇨ 1000ºC (NH_3)

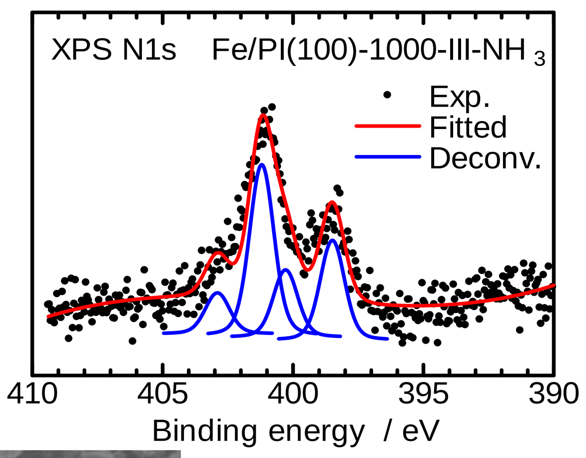




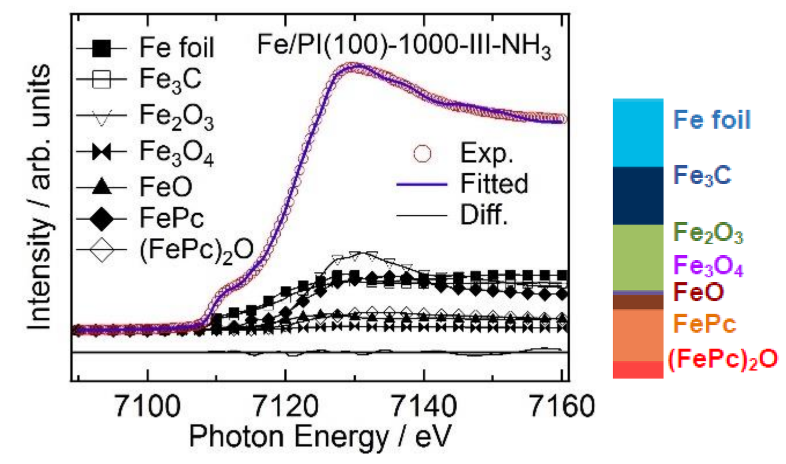
C: 90.9%, H: trace, N: 2.8%, Fe: 2.0%, BET: 1300 $m^2\ g^{-1}$



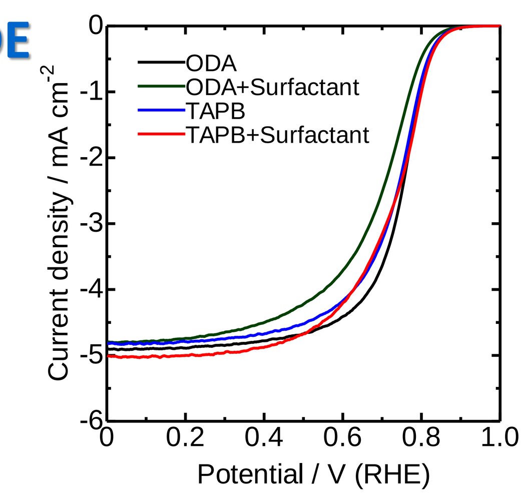
XPS



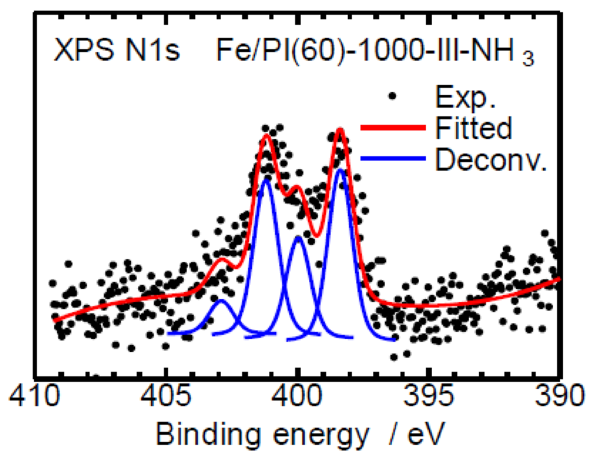
XAFS

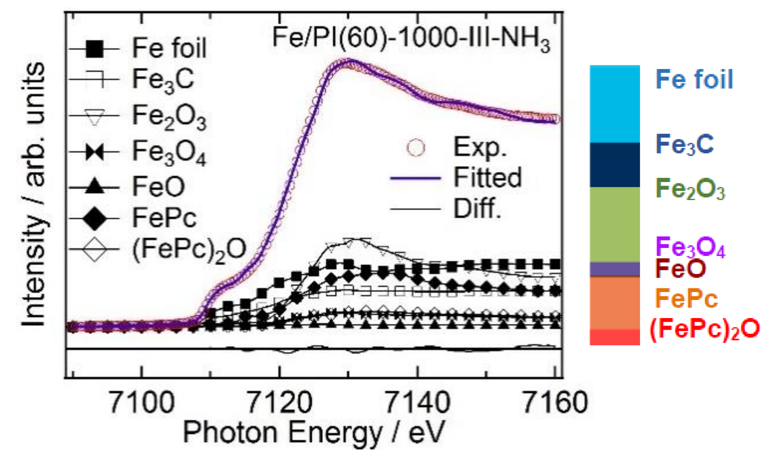


RDE



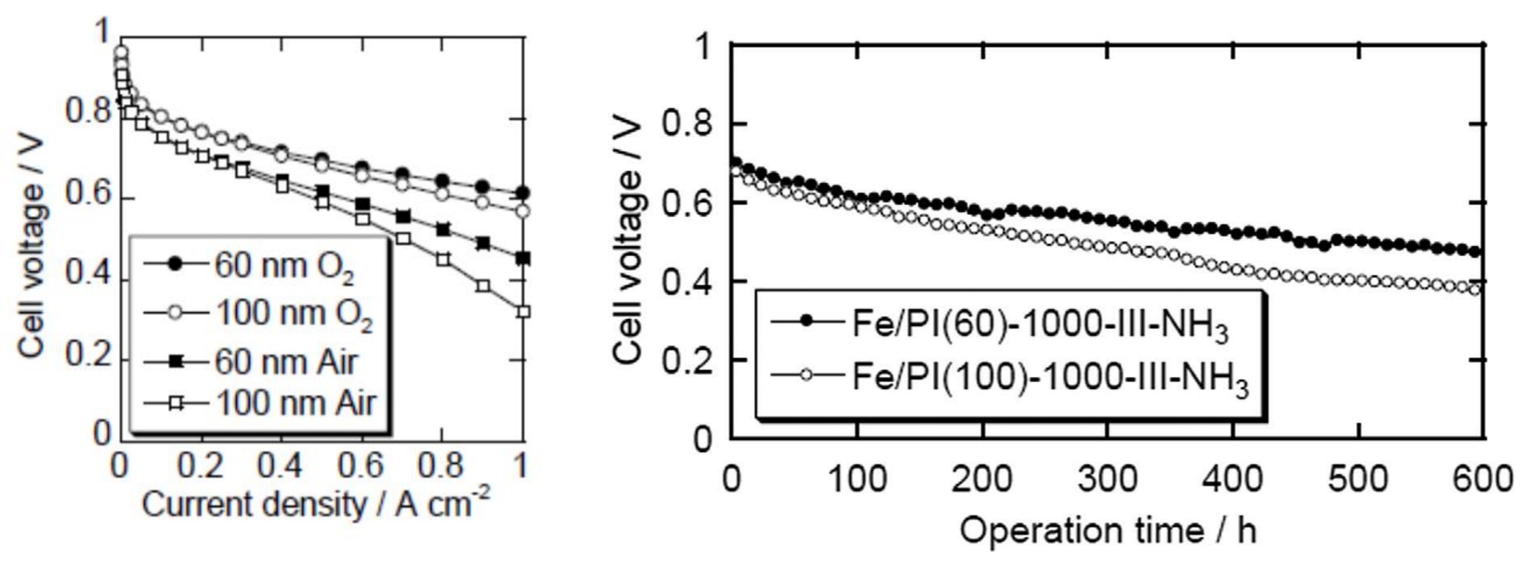
- Working Electrode (RDE): Catalyts/Glassy carbon(6φ) 0.2 mg/cm²
- Reference Electrode: RHE
- Counter Electrode: Carbon
- Electrolyte: O_2 saturated H_2SO_4 (0.5 M)
- Rotation: 1500 rpm





Y. Nabae et al, *Scientific Reports*, 2016, **6**, 23276.

Fuel Cell Testing



(left) I-V performance curves under 0.2 MPa atmosphere, and (right) durability curves measured at 0.2 A cm^{-2}. Anode: PtRu/C catalyst with 0.4 mg-PtRu cm^{-2} loading, humidified H_2 at 80° C. Cathode: 4 mg cm^{-2} catalyst loading, pure or balanced O_2 (humidified) at 80° C. Electrolyte: Nafion NR211. *T*: = 80° C.

Under pure oxygen: initial performance

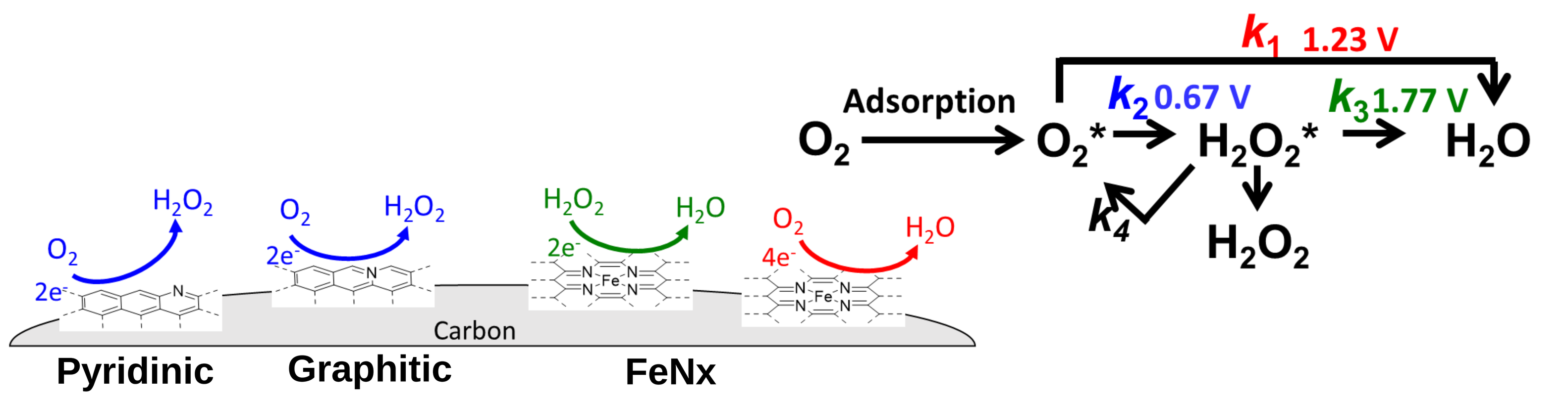
Group	Performance	Conditions	Reference
Our study	0.6 V@1 A cm^{-2}	I-V curves	J. Mater. Chem. (2014) 11561
J.P. Dodelet (Canada)	0.65 V@1 A cm^{-2}	0.5 mV/sec sweep	Nat. Commun. (2011) 416
P. Zelenay (US)	0.6 V@1 A cm^{-2}	-	Science (2017) 479
Nisshinbo-Ballard	0.58 V@1 A cm^{-2}	I-V curves	Sci. Adv. (2018) eaar7180

Under air: initial performance

Group	Performance	Conditions	Reference
Our study	0.46 V@1 A cm^{-2} 0.5 V @ 0.8 A cm^{-2}	I-V curves.	Sci. Rep. (2016) 23276
J.P. Dodelet (Canada)	0.5 V@0.7 A cm^{-2}	No I-V curves.	Nat. Commun. (2011) 416
S. Mukerjee (US)	0.44 V@1 A cm^{-2}	I-V curves	Energy Environ. Sci. (2016) 2418
Nisshinbo-Ballard	0.53 V@1 A cm^{-2}	I-V curves	Sci. Adv. (2018) eaar7180

Reaction Mechanism

- **Oxygen is reduced via 2+2 electron pathway rather than direct 4 electron pathway.**
  Azhagumuthu *et al*., *ACS Catal*., 5 5194 (2015).
  Azhagumuthu et al., J. Phys. Chem. C, 120 22515 (2016).
- **The first 2 electron reduction to H_2O_2 is sufficiently catalyzed by N-doped carbon.**
  Park *et al*., *ACS Catal*., 4 3749 (2014).
- **Small amount of Fe (may be FeNx site) increases the number of electron and onset potential.**
  Wu *et al*. Langmuir, 31 5529 (2015).



Conclusion

- A highly active NPM cathode catalyst was successfully synthesized by the pyrolysis of an Fe-containing polyimide precursor prepared from PMDA and TAPB.
- This catalyst demonstrates good fuel cell performance and promising durability, especially with air as the cathode gas.

This study is funded by NEDO

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