燃料電池デバイス及び電極触媒
Fuel cell device and electro-catalyst

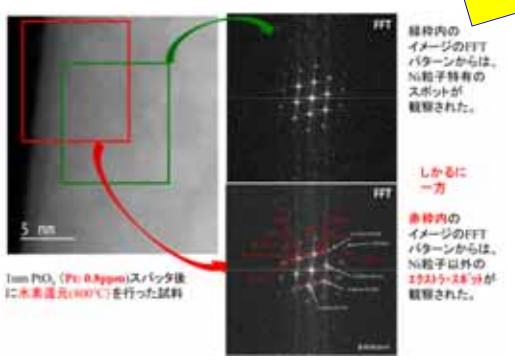
概 要 ﾏｲｸﾛｱﾅﾘｼｽと原子ﾚﾍﾞﾙｼﾐｭﾚｰｼｮﾝを組み合わせることで、中温域動作酸化物形燃料電池用ｱﾉｰﾄﾞ材料及び高分子形燃料電池用電極の設計を行った。 / High quality anode in intermediate temperature operation solid oxide fuel cells and high quality Pt electrode (and non-precious metal electrode) in polymer membrane fuel cells were designed by combination of microanalysis and atomistic simulation.

ヘテロ界面設計による高性能電極創製 ～微細構造観察と原子ﾚﾍﾞﾙｼﾐｭﾚｰｼｮﾝを組み合わせて～

微細構造解析結果と原子ﾚﾍﾞﾙのｼﾐｭﾚｰｼｮﾝの結果をもとに、高分子形燃料電池用省白金電極及び中温域動作固体酸化物形燃料電池用ｱﾉｰﾄﾞの設計を行った。

固体酸化物形燃料電池

微細構造観察 (PtO_x ｽﾊﾟｯﾀの例)

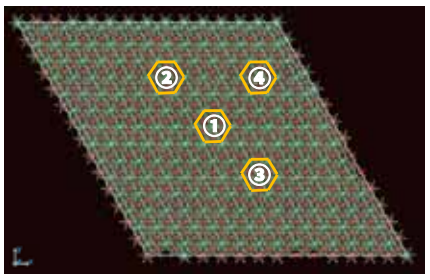


1nm PtO_x (Pt: 0.8ppm)スパッタ後に水素還元(600℃)を行った試料

表の格子間隔は測定値で、精度は小数点以下2桁

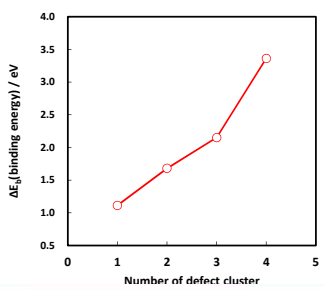
Diffraction spot	Lattice spacing / nm	Assigned materials and lattice plane
1	0.152	PtO (200)
2	0.230	Pt (200)
3	0.164	un-known
4	0.199	Pt (311), NiO (222)
5	0.200	Pt (200), Pt(111), Ni(111)
6	0.204	Pt(200), Pt (111), Ni(111), NiO(200)

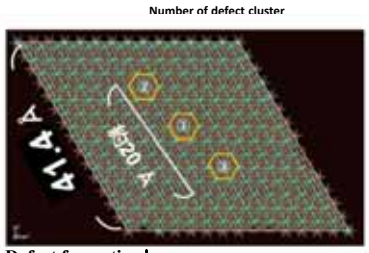
説明



Defect formation: $PtO \xrightarrow{NiO} V_{Ni}'' + Pt_i^{\cdot\cdot} + V_O^{\cdot\cdot} + O_i''$

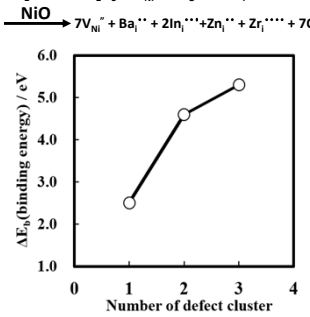
想定された表面欠陥構造



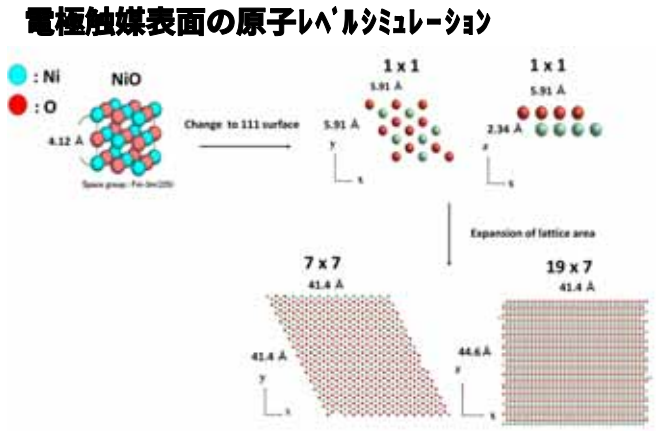


Defect formation:

$BaO + ZrO_2 + ZnO + In_2O_3 + Ni_{Ni}^{\times} + O_O^{\times} + 14V_i \xrightarrow{NiO} 7V_{Ni}'' + Ba_i^{\cdot\cdot} + 2In_i^{\cdot\cdot\cdot} + Zn_i^{\cdot\cdot} + Zr_i^{\cdot\cdot\cdot\cdot} + 7O_i'' + 7V_O^{\cdot\cdot}$

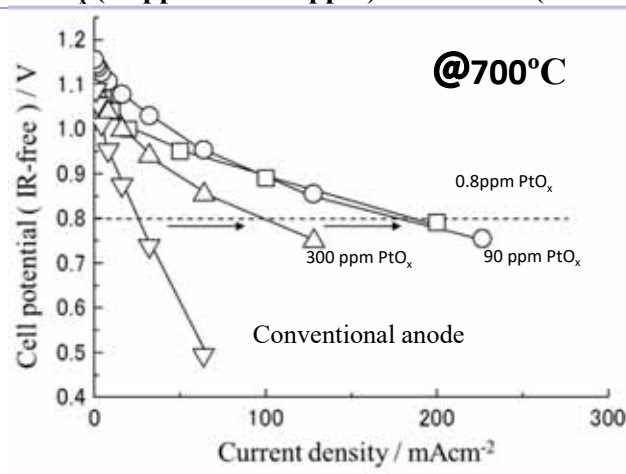


電極触媒表面の原子ﾚﾍﾞﾙｼﾐｭﾚｰｼｮﾝ



本研究のコンセプトに基づく酸化物形燃料電池(SOFC)中の界面設計によりｱﾉｰﾄﾞ性能は顕著に改善した。

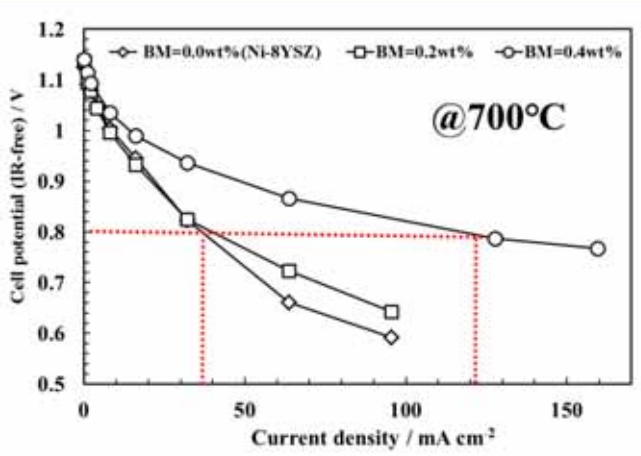
極微量PtO_x (0.8ppm から300ppm) ﾄﾞｰﾌﾟｻｰﾒｯﾄ(NiO-8YSZ)ｱﾉｰﾄﾞ



動作温度： 700ºC
ｱﾉｰﾄﾞ: NiO- 8YSZ cermet
ｶｿｰﾄﾞ: $La_{0.85}Sr_{0.15}MnO_3$
固体電解質: 8YSZ
ｶｿｰﾄﾞｶﾞｽ: O_2 (80 ml min^{-1})
ｱﾉｰﾄﾞｶﾞｽ： H_2 (80 ml min^{-1}, 70º saturation)

Fig. Comparison of IR-free performances observed for conventional anode and PtO_x doped anode in SOFCs,

0.4 wt% $Ba_2(In_{0.7}(Zr_{0.5}, Zn_{0.5})_{0.3})_2O_5$ ﾄﾞｰﾌﾟｻｰﾒｯﾄ(NiO-8YSZ)ｱﾉｰﾄﾞ



動作温度： 700ºC
ｱﾉｰﾄﾞ: NiO- 8YSZ cermet
ｶｿｰﾄﾞ: $La_{0.85}Sr_{0.15}MnO_3$
固体電解質: 8YSZ
ｶｿｰﾄﾞｶﾞｽ: O_2 (80 ml min^{-1})
ｱﾉｰﾄﾞｶﾞｽ： H_2 (80 ml min^{-1}, 70º saturation)

Fig. Comparison of IR-free performances observed for conventional anode and BM doped anode in SOFCs,

高分子形燃料電池

実施中プロジェクト：'TIA架け橋'

高性能白金電極の創製 ⇔ マイクロアナリシスと欠陥構造ｼﾐｭﾚｰｼｮﾝの融合 *ref 2,3

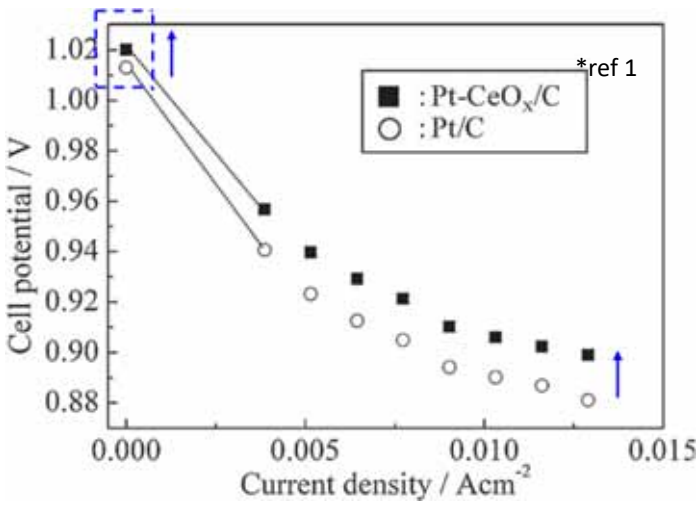


Fig. Fuel cell performances at 70°C;
Electrolyte: Nafion® (212) membrane , Anode gas: H_2 (80 ml min^{-1}, 70º saturation),
Cathode gas: oxygen (80 ml min^{-1} , 70º saturation), Pt content in cathode layer: 0.3mg_{Pt} cm^{-2}

非白金電極の創製 ⇔ 窒素ﾄﾞｰﾌﾟ炭素触媒 *ref 4

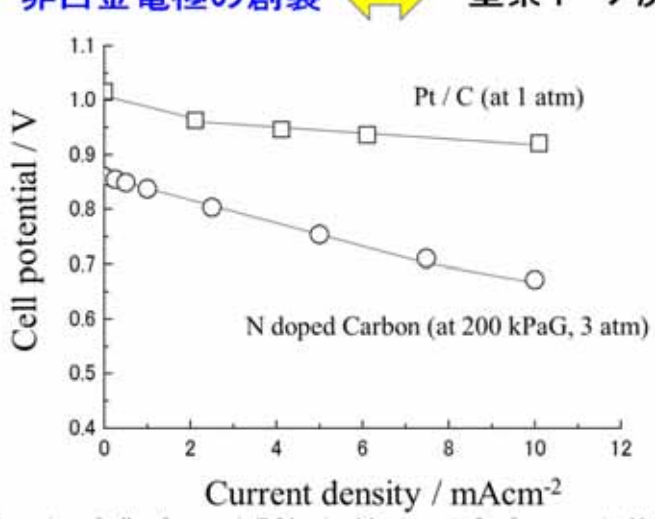


Fig. Comparison of cell performance in Tafel region. Measurement of performance using N doped carbon was performed at 200 kPaG (3 atm). Also, measurement of cell performance of Pt / C (Pt content in cathode: 0.3 $mg_{Pt}cm^{-2}$).
Electrolyte: Nafion® (212) membrane, anode gas: humidified H_2 (80 ml min^{-1}, 70º saturation),
and cathode gas: oxygen (80 ml min^{-1}, 70º saturation). Operation temperature: 70°C.

Ref 1 : Fugane K, Mori T, Yan P F, Masuda T, Yamamoto S, Ye F, Yoshikawa H, Auchterlonie G and Drennan J, 'Defect structure analysis of hetero-interface between Pt and CeO_x promoter on Pt electro-catalyst', **ACS Applied Materials & Interfaces,** Vol.7(4), pp.2698-2707(2015).
Ref. 2: Chauhan S, Mori T, Masuda T, Ueda S, Richards G, Hill J, Ariga K, Isaka N, Auchterlonie G, and Drennan J, 'Design of low Pt concentration electro-catalyst surfaces with high oxygen reduction reaction activity promoted by formation of heterogeneous interface between Pt and CeO_x nanowire', **ACS Applied Materials & Interfaces,** Vol.8(14), pp.9059-9070(2016).
Ref. 3: Fugane K, Mori T, Ou D R, Suzuki A, Yoshikawa H, Masuda T, Uosaki K, Yamashita Y, Ueda S, Kobayashi K, Okazaki N, Matolinova I and Matolin V, 'Activity of oxygen reduction reaction on small amount of amorphous CeO_x promoted Pt cathode for fuel cell application,' **Electrochimica Acta**, Vol.56(11), pp.3874-3883(2011).

Ref 4 : Zhang Y J, Fugane K, Mori T, Niu L, and Ye J, 'Wet chemical synthesis of nitrogen-doped graphene towards oxygen reduction electrocatalysts without high-temperature pyrolysis ', **Journal of Materials Chemistry**, Vol.22(14), pp.6575-6580(2012). / Zhou Z, He F, Shen Y, Chen X, Yang Y, Liu S, Mori T, and Zhang Y, **Chem. Commun**., DOI: 10.1039/C6CC09442B (2017).

‡TIA 架け橋プロジェクトメンバー： 筑波大学(中村潤児研究室、リーダー：中村潤児教授), NIMS (リーダー：森上席研究員), AIST, KEK, 東京大学物性研

中村教授の研究成果の例： Donghui Guo, Riku Shibuya, Chisato Akiba, Shunsuke Saji, Takahiro Kondo, Junji Nakamura, 'Active sites of nitrogen-doped carbon materials for oxygen reduction reaction clarified using model catalysts', Science, 351, pp. 361-365 (2016). / NATURE NANOTECHNOLOGY | RESEARCH HIGHLIGHTS doi:10.1038/nnano.2016.36Published 03 March 2016.

NIMS ｴﾈﾙｷﾞｰ・環境材料研究拠点
森 利之、鈴木 彰、伊藤滋啓、大久保 弘
問い合わせ先：MORI.Toshiyuki@nims.go.jp