

第134回定例研究会 資料5

アンモニア利用燃料電池の可能性

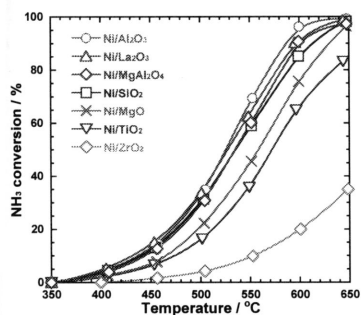


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第134回定例研究会
「古くて新しい水素媒体～アンモニア特集」

担持Ni触媒のアンモニア分解活性



活性	Catalysts	BET surface area of supports (m ² /g)
高	Ni/Al ₂ O ₃	201
	Ni/La ₂ O ₃	5
	Ni/MgAl ₂ O ₄	47
	Ni/SiO ₂	279
	Ni/MgO	47
	Ni/TiO ₂	47
低	Ni/ZrO ₂	7

La₂O₃, MgAl₂O₄ BET表面積: 小
Ni/La₂O₃, Ni/MgAl₂O₄ 活性: 高

Fig. Ammonia conversion for ammonia decomposition over 10 wt.% Ni catalysts supported on (○) Al₂O₃, (△) La₂O₃, (◇) MgAl₂O₄, (□) SiO₂, (×) MgO, (▽) TiO₂, and (◊) ZrO₂.

La添加効果

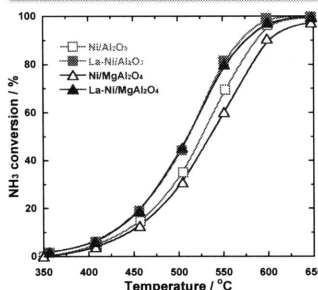


Fig. Ammonia conversion for ammonia decomposition over (□) 10 wt.% Ni/Al₂O₃, (■) 2.3 wt.% La-9.8 wt.% Ni/Al₂O₃, (△) 10 wt.% Ni/MgAl₂O₄, and (▲) 2.3 wt.% La-9.8 wt.% Ni/MgAl₂O₄.

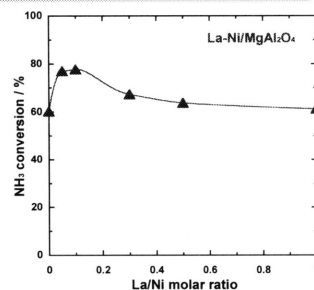
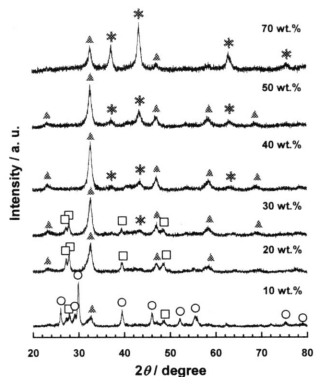


Fig. Ammonia conversion as a function of La/Ni molar ratio for ammonia decomposition over La-Ni/MgAl₂O₄ at 550 °C. Reaction conditions: NH₃ 100%, S.V. = 6,000 l kg⁻¹ h⁻¹.

La添加効果: Ni/MgAl₂O₄ > Ni/Al₂O₃

最適値: La/Ni = 0.1

XRDパターン(10-70 wt.% Ni/La₂O₃)



* NiO ▲ LaNiO₃
○ La₂O₃ □ La(OH)₃

> Ni担持量: 10 → 40 wt.%
La₂O₃, La(OH)₃の消失
LaNiO₃ピーク強度の増大
NH₃転化率の上昇

> Ni担持量: 40 → 70 wt.%
LaNiO₃ピーク強度の低下
NiOピーク強度の増大
NH₃転化率の減少

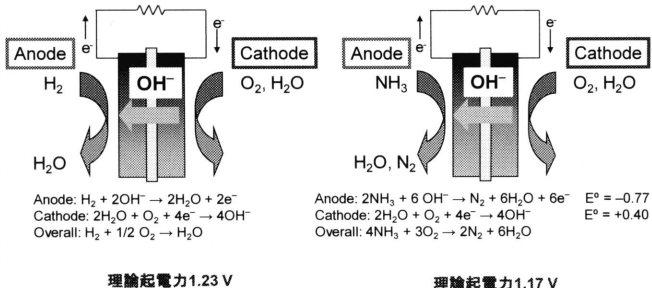
LaNiO₃の生成が活性に影響

還元
LaNiO₃ → 高分散Ni/La₂O₃

Fig. XRD patterns of 10-70 wt.% Ni/La₂O₃ calcined at 600 °C.

アニオン交換膜燃料電池

- アニオン交換膜
- ✓ 4級アンモニウム塩基などのイオン交換基をもつ炭化水素系ポリマー
- ✓ 水を膜中に保持し、OH⁻伝導性を持つアルカリ性電解質
- ✓ K⁺などのカチオンを含まず、炭酸塩の析出が起きない
- ✓ 電極に貴金属が不要



アニオン交換膜へのCO₂の影響

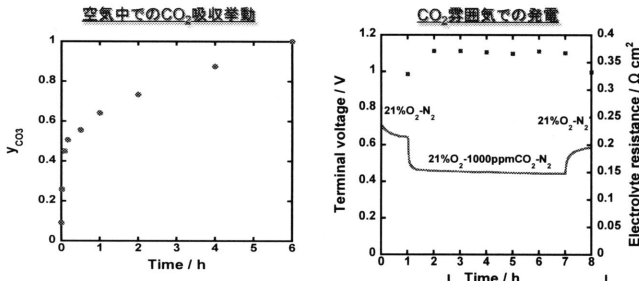


Fig. Time course of y_{CO_2} of OH⁻ form anion exchange membrane in ambient air at 20°C. $y_{CO_2} = ([CO_3^{2-}]_m + [HCO_3^-]_m) / (IEC)$ Where $[CO_3^{2-}]_m$ and $[HCO_3^-]_m$ are the concentration of CO_3^{2-} and HCO_3^- in anion exchange membrane. IEC = ion-exchange capacity [mol / cm³]

Fig. Time course of terminal voltage and electrolyte resistance of anion exchange membrane fuel cell. Operating temperature: 50 °C, anode gas: H₂ (humidified at 50°C), cathode gas: 21% O₂ - N₂ or 21% O₂ - 0.1% CO₂ - N₂ (humidified at 50°C).

アニオン交換膜へのNH₃の影響

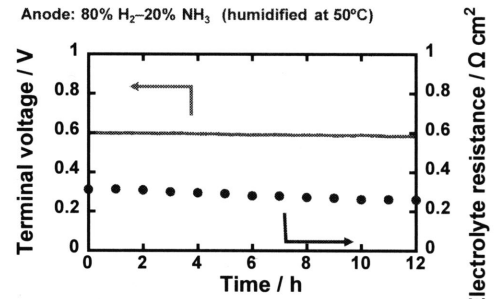


Fig. Time course of terminal voltage and electrolyte resistance of anion exchange membrane fuel cell. Operating temperature: 50 °C, anode gas: NH₃ - H₂ (humidified at 50°C), cathode gas: O₂ - N₂ (humidified at 50°C).

直接アンモニア燃料電池; OCV低下現象

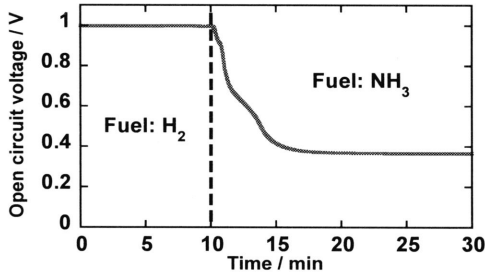


Fig. Time course of open circuit voltage of anion exchange membrane fuel cell. Operating temperature: 50 °C, anode gas: NH₃ (humidified at 50°C), cathode gas: O₂ - N₂ (humidified at 50°C).

直接NH₃燃料電池の発電特性

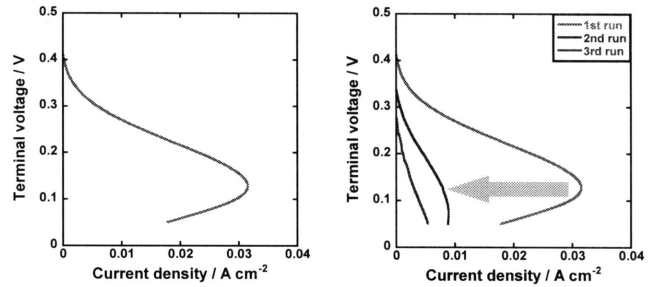


Fig. I-V characteristics of anion exchange membrane fuel cell. Operating temperature: 50 °C, anode gas: NH₃ (humidified at 50°C), cathode gas: O₂-N₂ (humidified at 50°C), scanning rate: 1 mV sec⁻¹.

Fig. I-V characteristics of anion exchange membrane fuel cell. Operating temperature: 50 °C, anode gas: NH₃ (humidified at 50°C), cathode gas: O₂-N₂ (humidified at 50°C), scanning rate: 1 mV sec⁻¹.

NH₃酸化反応の電位依存性 (Pt/C)

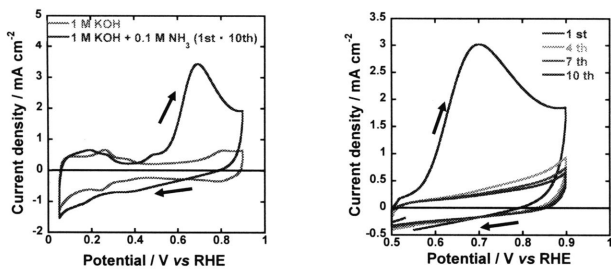
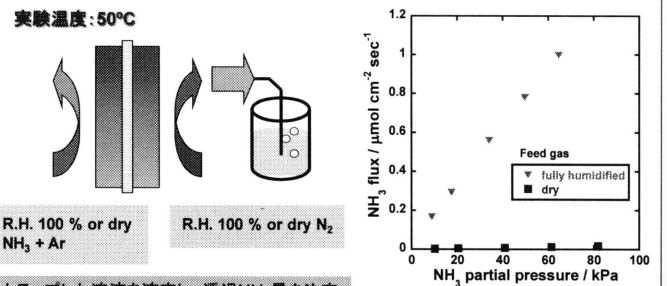


Fig. Cyclic voltammogram of Pt/C in the presence (blue line) and absence (red line) of 0.1 M NH₃ in 1 M KOH at 25°C with a scanning rate of 20 mV s⁻¹.

Fig. Cyclic voltammogram of Pt/C in (1 M KOH + 0.1 M NH₃) at 25°C with a scanning rate of 20 mV s⁻¹.

Pt表面へのN_{ad}の蓄積による電流値の減少

アニオン交換膜のNH₃透過性



実験温度: 50°C

R.H. 100% or dry NH₃ + Ar

R.H. 100% or dry N₂

トラップした溶液を滴定し、透過NH₃量を決定

Dryのガス供給時に比べて加湿ガス供給時には約80倍のNH₃透過

Fig. NH₃ flux across anion exchange membrane at 50°C as a function of NH₃ feed pressure.