〔数 理 科〕

〔区 分 A〕

矢野　潤

# Electrocatalytic Activity of Metal－Polyaniline Film Electrodes for Direct Methanol Fuel Cell

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In order to develop better and cheaper electrocatalysts for the oxidation of methanol and the reduction of dissolved oxygen in direct methanol fuel cells (DMFCs), several combinations of a conductive polymer polyaniline (PANI), dispersed Pt particles and pre-dispersed metal particles such as Sn and Fe were examined.　Both the cathodic current for the oxygen reduction ($i_{ox}$) and the anodic current for the methanol oxidation ($i_{MeOH}$) showing the electrocatalytic activity of the Pt particles were remarkably enhanced when the particles were dispersed on PANI films.　The activity strongly depended on the morphology and the electric conductivity of the five PANI films with different dopant anions: $SO_4^{2-}$, $NO_3^-$, $ClO_4^-$, $BF_4^-$ and $Cl^-$.　The highest activity was achieved for the $SO_4^{2-}$-doped PANI film.　When the dispersed Pt particle $SO_4^{2-}$-doped PANI film was employed, the $i_{ox}$ value was almost twice and the $i_{MeOH}$ value became 6.16 times as large as that observed using a dispersed Pt particle carbon electrode without the PANI film.　The much higher electrocatalytic activity for the methanol oxidation was probably due to not only the greater surface areas of the PANI film for the dispersed particles, but also the adsorption of the intermediate species such as CO onto the PANI molecules.

To reduce the dispersed amount of the expensive Pt particles, inexpensive base metal particles were pre-dispersed on the PANI film, and the Pt particles were dispersed on the film.　Among the pre-dispersed metal particles attempted here (Sn, Cu, Cr, Ni, In, Co, Sb, Bi, Pb, Mn and Fe), the highest activity was obtained with Sn particles for the methanol oxidation and with Fe particles for the oxygen reduction.　When the ratio of dispersed Pt to Sn particles ranges from 32：68 to 100：0, $i_{MeOH}$ is higher than that measured with the dispersed Pt particle PANI films without the Sn particles.　This meant that utilizing dispersed Sn particles could reduce the dispersed amount of the Pt particles.　On the other hand, in the oxygen reduction, it was practically significant that 83% of the Pt particles could be replaced by the inexpensive Fe particles.
83% of the Pt particles could be replaced by the inexpensive Fe particles.

矢野　潤

# Polyaniline Film as a Metal Free Electrocatalyst for the Anode Reaction of the Direct Ascorbic Acid Fuel Cells

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A conductive polymer, polyaniline (PANI), was electrodeposited on a glassy carbon electrode. Using this PANI-modified electrode, L-ascorbic acid was electro-oxidized, and the electrocatalytic activity of PANI was evaluated for 1) the effect of preparation conditions of PANI, 2) the durability

of catalytic action and 3) the effect of metal deposition.    The highest electrocatalytic activity was obtained with $SO_4^{2-}$-doped PANI.    The durability of the catalytic action was significantly improved by the PANI modification.    The metal deposition deactivated rather than activated the PANI-modified electrode.    The PANI-modified electrode was regarded as a promising anode for the direct ascorbic acid fuel cell because it was known to be a highly active toward the electro-oxidation of L-ascorbic acid for a long time and was entirely free from harmful heavy metals and expensive Pt.

### 松田　一秀

**Rational Solutions of the Sasano System of Type A^{(2)}_5, K.MATSUDA,**

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SIGMA 7 (2011), (http://www.emis.deZjoumals/SIGMA/2011/030/sigma11-030・pdf)

　A^{(2)}_5型のアフィン・ワイル群の対称性を持つ,笹野系と呼ばれる微分方程式系の有理関数解を、ベックルント変換を用いて完全に分類した。

## 〔区　分　B〕

### 矢野　　潤

### これでわかる化学演習

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これでわかる化学演習（三共出版）(2011)

　高等専門学校、短期大学、大学の基礎教養の化学の教科書で、わかりやすさを最優先した既刊の「これでわかる化学」の各章に完全に対応した例題、問題、演習問題を設けた演習書として作成した。図を豊富に挿入して例題の理解を深めた後に問題を解き、実力アップのための演習問題につながるような構成とした。項目は以下のとおりである。従来にはない基礎の確認や章末課題などを配し、図解、問題や例題の図解など解り易さを最優先して以下の項目を詳述した。

はじめに
1.物質の構成
2.化学式と物質量
3.化学結合
4.物質の三態
5.希薄溶液の性質
6.化学変化と反応熱
7.酸と塩基
8.酸化と還元
9.酸化還元と電気
付録.単位と有効数字

### 安里　光裕

### 解析力学の基礎

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技術評論社(2010年8月)

理工系の大学生、および、高専生、高専専攻科生を対象とした、解析力学の基礎を理解するための教科書である。第１章：解析力学を学ぶための準備、第２章：ラグランジュの運動方程式、第３章：変分原理とハミルトンの原理、第４章：ハミルトンの正準方程式。

## 〔区 分 Ｅ〕

矢野　　潤

### Pt and Sn dispersed polyaniline film-covered electrodes for a direct ethanol fuel cell

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Although direct methanol fuel cells (DMFCs) are promising fuel cells, they have at least five problems before practical use is achieved: (A) expensive electrocatalysts such as Pt are required for methanol oxidation and the electrocatalytic activity is relatively low; (B) the adsorption of reaction intermediates deactivates the electrocatalysts; (C) electroreduction of dissolved oxygen should be promoted; (D) high methanol crossover through the polymer membrane greatly decreases the cell voltage and methanol utilization; (E) the toxicity of methanol has the risk of causing serious problems. To alleviate these problems, we employed metal-dispersed polyaniline (PANI) as the electrocatalyst and ethanol as the fuel. The affinity of PANI for organic compounds is expected not only to suppress the deactivation of metal catalysts by adsorption of the reaction intermediates but also to function as an electron-mediated electrocatalyst itself. On the other hand, ethanol has less toxicity and permeability through the polymer membrane than does methanol. The PANI film could act as a porous matrix on which the metal electrocatalysts are dispersed. The dispersion can decrease the poisoning effect as well as the amount of the precious Pt electrocatalyst needed. We also reported that the PANI film effectively promotes the electroreduction of dissolved oxygen. In addition to its role as a porous matrix, the PANI film itself could function as an electrocatalyst. In this paper, to effectively electro-oxidize ethanol, the following subjects were investigated using electrochemical measurements. 1) Effect of electropolymerization condition of the PANI film (dopant anion and film thickness), 2) effect of metal dispersion, and 3) durability of catalytic activity.

矢野　　潤

### Metal-dispersed polyaniline electrodes for the anodes of the direct ethanol fuel cell

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To develop better and less expensive electrocatalysts for the oxidation of ethanol in direct ethanol fuel cells, several combinations of a conductive polymer polyaniline (PANI), dispersed Pt

particles and pre-dispersed metal particles, such as Sn and Fe, were examined.    The anodic current for the ethanol oxidation ($i_{EtOH}$) that provides the electrocatalytic activity of the Pt particles was remarkably enhanced when the particles were dispersed on PANI films.    The activity strongly depended on the morphology and the electrical conductivity of the five PANI films with different dopant anions: $SO_4^{2-}$, $NO_3^-$ and $Cl^-$.    The highest activity was achieved for the $SO_4^{2-}$-doped PANI film. To reduce the dispersed amount of the expensive Pt particles, inexpensive base metal particles were pre-dispersed on the PANI film, and the Pt particles were then dispersed on the film.    Among the investigated pre-dispersed metal particles (Sn, Cu, Zn and Fe), the highest activity was obtained with Sn particles for the ethanol oxidation.    When the ratio of the dispersed Pt to Sn particles ranged from 10: 90 to 100:0, $i_{EtOH}$ was higher than that measured with the dispersed Pt particle PANI films without the Sn particles.    This meant that utilizing dispersed Sn particles could reduce the dispersed amount of the Pt particles needed.

矢野　　潤

## Conductive Polymers as Color Display Materials

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 Conductive polymers have useful and interesting properties other than their electronic conductivity.    One of the most useful properties is their color change originated from their oxidized state.    Two conductive polymers, polyaniline (PANI) and poly($o$-phenylenedi- amine) (PoPD), have also various oxidized states from a fully reduced state to a fully oxidized state. In the fully reduced state, the polymers are colorless.    As the polymers are electrochemically oxidized and the oxidized levels become higher, they gradually color bright green for PANI and vermilion for PoPD.    It is well-known that this behavior is applicable as an electrochromic display (ECD).    The fully reduced PANI and PoPD gradually color when they are exposed to air because they could be oxidized by oxidation, which can functions as time displays.    Besides, the color tones of the oxidized polymers vary in solution pH because the polymers have acid-base equilibrium.    This is expected to act as optical pH sensors.

 Both PANI and PoPD have conductive porous network structures with positively charged sites, and they can incorporate with Prussian Blue (PB) and an anionic quinone, 1-amino-4- bromoanthraquinone-2-sulfonic acid (BA), whose colors can also be changed to another colors by the variation of the oxidation levels.    Two composite polymers can be prepared as multicolor expressible display materials: PoPD/PB and PANI/BA.    The composite polymers separately retain the color change properties of each component and there is no undesirable interference.    The color change as ECDs are as follows: colorless-vermilion- green for PoPD/PB and colorless-green-purple for PANI/BA.    These composite polymers are also expected to be applicable as new type ECDs, time displays and optical pH displays.

柳井　　忠
授業におけるＷｅｂシステムの利用（２）

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　高専学生の家庭学習の補助として、平成１９年度から行っているＷｅｂシステムを利用した学生への情報提供について、平成２０年の大会で行った初年度における成果と分析の報告に続き、その後の２１年度までの３年間の経過と利用状況の推移、学生へのアンケート結果を報告し、分析と今後の課題の考察を行った。

　従来のプリント配布より多くの情報を提供できること、初年度より利用頻度は上がって学生への普及は進んでいること、学生の利用のしかたに対する指導が課題であることなどを述べ、２２年度に新たに提供した教材についても報告した。

## 安里　光裕

### 鉄中のＰＡＣプローブと不純物の相互作用エネルギーと格子歪の第一原理計算Ⅱ

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日本金属学会2010年秋季大会(北大)2010年9月27日

　我々のグループでは、現在、添加元素をFe(母体元素)に対する不純物原子として扱い、Fe中の不純物原子間相互作用エネルギーをフルポテンシャルKKR-Green関数法の高精度第一原理計算を用いて算出し、周期表に沿ってデータベース化し、あわせて、相互作用のメカニズムを解明するという試みを行っている。

　Fe中の不純物原子間相互作用エネルギーは、実験的には、PAC原子核実験で高精度に求められており(Hyper助e lntteractions60(1990),581-597)、前回、不純物原子周りの格子歪効果を無視したFe中のPACプローブ(Sn)と不純物原子(Al,Co〜Ge,Rh,Pd)の相互作用エネルギーの計算、および、I個の不純物原子の周りの格子歪を扱った予備的な計算の結果について報告した。今回は、その後の研究の進展状況について報告した。具体的には、2個の不純物原子の周りの格子歪効果を取り入れた計算の取扱いとその結果について報告し、実験値を定量的にどれくらい再現できるのかを示した。

## 安里　光裕

### Screened-FPKKR法による遷移金属シリサイドXSr(X=Ti〜Cu)の電子構造・磁性

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日本金属学会2010年秋季大会(北大)2010年9月27日

スピントロニクス、熱電変換の材料として、遷移金属シリサイドXSiが期待されている。実験的には、B20構造のXSiは、X=Feは半導体非磁性、X=Mnは金属強磁性、X=Coは金属非磁性となる。また、FeSiにCoを添加すると、強磁性になることも知られている。これらの合金の磁性のX依存性をScreed-FPKKR法(GGA,LSDA)の第一原理計算で調べ、統一的に明らかにした。

## 原田　潤平

### 対称性の自発的破れによる超流動ヘリウム４の研究：転移温度とロトンギャップ

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応用物理学会中国四国支部、日本物理学会中国支部・四国支部、日本物理教育学会中国四国支部、2010年度支部学術講演会、高知大学朝倉キャンパス　2010年7月31日

　対称性の自発的破れにもとづいて、ハードコア相互作用するボース粒子系の２次相転移温度の表式を導出し、転移温度が３つのパラメータ(ボース粒子の質量、粒子数密度、ボース粒子の硬殻直径)だけで決まっ

ていることを示す。得られた転移温度の表式を液体ヘリウム４に適用すると、２次相転移温度の理論値は2.194Kとなり、λ温度の実験値と1%以下の精度で一致する。さらに、絶対零度におけるロトンのエネルギーギャップを計算し、エネルギーギャップと入温度の比が4であることを示す。この比から得られるロトンのエネルギーギャップの値は、絶対零度において8.707Kとなり、実験から得られた値8.712Kとのずれは0.1%以下であることを報告する。