Reduction of NOx with NH$_3$ in the Presence of Pyrolyzed Macro-cycle Catalyst

E. Björnbom, O. Lindström, S. Järås, P. Björnbom, M. Majari, T. Kaimakis, Y. Kiros

Department of Chemical Engineering and Technology, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Abstract
Reduction of NOx with NH$_3$ in the presence of pyrolyzed cobalt-tetraphenylporphyrin, CoTPP “macrocycle black”, was studied. Active carbon, Norit RBXS 1 was used as a carrier. The experimental conditions were varied as follows: temperature from 95 to 140 °C, space velocity of the gas mixture 1000-5000 h$^{-1}$ and catalyst content 0 to 1%. The results showed that, in the experimental range studied, the temperature has no significant effect on the conversion of NOx. The conversion of NOx at low space velocity of the gas (1000 h$^{-1}$) was high (approx. 90%) both in the presence and absence of CoTPP black. This was explained by the fact that the active carbon used as a catalyst support has a catalytic effect on the reduction of NOx. At low space velocity, this effect is sufficient to achieve high conversion of NOx in the presence of active carbon only. The conversion decreased at higher space velocity, however. The presence of CoTPP black counteracted the negative effect of the increased space velocity. The effect of the “macrocycle black” on the conversion of NOx was significant at higher space velocities.

Keywords: Nitrogen oxide reduction, ammonia, catalytic, active carbon, porphyrin.

Acta Polytechnica Scandinavica, 197 (1991) 1-14

Pyrolyzed macrocycles on high surface area carbons for the reduction of oxygen in alkaline fuel cells

Y. Kiros* and S. Schwartz
Royal Institute of Technology, Department of Chemical Technology, S-100 44 Stockholm Sweden

Abstract
Polarization characteristics and preparation methods of double-layer porous gas diffusion electrodes on various carbon materials in alkaline fuel cells were investigated. The electrodes with active carbon carriers were catalyzed with cobalt/iron tetraphenylporphyrin or silver. These electrodes show a potential of $-186$ mV (versus Hg/HgO) at 1.0 A/cm$^2$ when operated with oxygen at 40 °C and 5 M KOH. Various techniques such as surface area measurements, scanning (SEM) and transmission (TEM) electron microscopy in combination with energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS) were used to characterize the structure and morphology of the catalyst layer.

Journal of Power Sources 45 (1991) 547-555

Cobalt and cobalt-based macrocycle blacks as oxygen-reduction catalysts in alkaline fuel cells

Y. Kiros*, O. Lindström and T. Kaimakis
Royal Institute of Technology, Department of Chemical Technology, 100 44 Stockholm Sweden

Abstract
The electrochemical reduction of oxygen on high surface area carbons catalyzed by cobalt and pyrolyzed macrocycles has been studied in alkaline fuel cells. Tests were also carried out with ‘green black’, i.e.,
pyrolyzed phyto-biomass. Galvanostatic polarization curves show that cobalt from cobalt acetate and fine cobalt metal power exhibit a high catalytic activity. The activity of pyrolyzed cobalt tetraphenylporphyrin (CoTPP) is due to the combined effects of the cobalt additive and the charred residue of the macrocycle. ‘Green black’, with chlorophyll as macrocycle black precursor, has a similar effect. The dissolution of cobalt from the electrode surface has been established. Life tests with these electrodes are reported.

Journal of Power Sources 45 (1993) 219-227

Separation and permeability of zincate ions through membranes
Yohannes Kiros
Royal Institute of Technology, Department of Chemical Engineering and Technology Chemical Technology, 100 44 Stockholm, Sweden

Abstract
A novel method for the separation of zincate ions in alkaline media has been developed. This development uses a precipitation reaction of Mn(OH)2 and application on a microporous separator (Celgarde). The amount of zinc, passed through the membranes was estimated by electrogravimetric method. Different inorganic materials in combination with the separator material have been tested. Effective low grade, permeability of zincate ions and increased resistivities have been found to be related to the amount of Mn(OH)2 applied on the separator.

Keywords: Separation; Permeability; Membranes; Zinc; Manganese


Electrocatalytic Properties of Co, Pt, and Pt-Co on carbon for the Reduction of Oxygen in Alkaline Fuel Cells
Yohannes Kiros
Department of Chemical Engineering and Technology, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Abstract
The effect of cobalt, platinum, and cobalt-platinum alloys on high surface area carbons for oxygen reduction in alkaline electrolyte was investigated. The Pt-Co catalyst with ca. 1:3 atomic ratio was prepared by addition of H2PtCl6 solution to a mixture of methanol and a 5% surfactant in deionized water containing cobalt acetate and carbon suspension. This was followed by drying and heat-treatment at 700 and 900 °C in a flow of hydrogen and nitrogen gas mixtures. Polarization curves and kinetic parameters for Pt, Co and Pt-Co were conducted and compared in 6M KOH and 80 °C. Higher activities were observed for the Pt-Co alloy that had been heat-treated at 900 °C. In addition to increased activity of this catalyst, the unalloyed base metal (Co) contributes to total performance improvement of the oxygen reduction process. Furthermore, surface, structural and chemical characterizations of the catalysts were carried out using transmission electron microscopy, x-ray diffraction, Brunauer, Emmet and Teller method and atomic absorption spectroscopy. Dissolution of cobalt from the electrodes, both from the single cobalt phase and Pt-Co alloy catalysts, has been established. The x-ray results demonstrated a shift to lower lattice parameters (3.618 Å) by the Pt-Co alloys, prepared at 900 °C than the pure platinum catalyst (3.919 Å).

Journal of the Electrochemical Society 143 (1996) 2152-2157
Long-term hydrogen oxidation catalysts in alkaline fuel cells
Y. Kiros*, S. Schwartz

Abstract
Pt-Pd bimetallic combination and Raney Ni catalysts were employed in long-term electrochemical assessment of the hydrogen oxidation reaction HOR in 6 M KOH. Steady-state current vs. potential measurements of the gas diffusion electrodes have shown high activity for these types of catalysts. Durability tests of the electrodes have shown increased stability for the Pt/Pd-based catalysts than the Raney Ni at a constant load of 100 mA/cm² and at temperatures of 55 °C and 60 °C, respectively. Surface, structural and chemical analyses by BET surface area, transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) were used to characterize the composite electrode/catalyst both before and after the electrochemical testing.

Keywords: Hydrogen oxidation; Platinum; Palladium; Bimetal; Raney Ni; Alkaline fuel cell

Effects of carbon pretreatment for oxygen reduction in alkaline electrolyte
Massoud Pirjamali, Yohannes Kiros

Abstract
The effects of different media on carbon pretreatments for oxygen reduction in alkaline electrolyte without application of active electrocatalysts were examined. Low surface area Vulcan XC-72 and high surface area Ketjenblack EC-300 were subjected to aqueous acid (fluoric or formic), gaseous (H₂, N₂ or CO₂) and thermal treatments at 600 or 900 °C. Though non-scrubbed air was used, as a result of which carbonate build-up was high and peroxide concentration increased due to the electrode reaction, some of the electrodes resulted in life-tests of more than 2000 h at 65 °C, 6 M KOH with a constant load of 50 mA cm² and intermittent polarisations at higher current densities. BET-surface areas and pH changes of more than 60% and weight losses of up to 15% of the carbon blacks were observed after the pretreatment steps. Electrochemical characterisation of the carbons showed that pretreatment steps of the carbon blacks have a significant effect on the long-term stability and activity of the gas diffusion electrodes in alkaline electrolyte.

Keywords: Carbon pretreatment; Alkaline electrolyte; Gas diffusion electrodes; Physical and surface characterisation; Activity; Stability
Electrode R&D, stack design and performance of biomass-based alkaline fuel cell module

Y. Kiros a*, C. Myrén a, S. Schwartz a, A. Sampathrajan b, M. Ramanathan b

a Department of Chemical Engineering and Technology, Chemical Technology, KTH-Royal Institute of Technology, S-100 44 Stockholm, Sweden
b Department of Bio-Energy, College of Agricultural Engineering, Tamil Nadu Agricultural University (TNAU), Coimbatore, India

Abstract
Electrode formulations with different materials and manufacturing techniques were tested electrochemically in order to assess their stability and activity in long-term operations. Cathode electrocatalysts such as CoTPP, Ca_{0.9}La_{0.1}MnO_3 and Pt-Co alloys were incorporated in high surface area carbons and operated at a constant load of 100 mA/cm^2, 80 °C and an electrolyte concentration of 5 M KOH. Similarly, anode catalysts with Pt-Pd bimetallic combinations were also tested and ascertained in half-cell measurements. Surface area measurements and Transmission Electron Microscopy (TEM) analyses were carried out both before and after the electrochemical test procedures. The electrodes were incorporated into a seven and two cell module design of the external and internal manifolding types and the experiences gained from these design principles are described, respectively. Furthermore, a biomass fed AFC module with all the system descriptions, steps, and a demonstration layout of producer gas to alkaline fuel cell are examined and discussed. Wood charcoal and agro-residues were used as feedstock and as a primary fuel. Power output of the different feedstock in a producer gas fed alkaline fuel cell has the shown potentiality and efficiency to be applied as a stand-alone power generator.


Cost-effective Perovskite for Intermediate Temperature Solid Oxide Fuel Cells (ITSOFC)

Y. Kiros, X. R. Liu, B. Zhu

Department of Chemical Engineering and Technology, Chemical Reaction Engineering, Royal Institute of Technology (KTH ), S- 100 44 Stockholm, Sweden

Abstract
Low lanthanum containing perovskite, Ca_{0.9}La_{0.1}MnO_3 (CLM) was synthesized. The material was characterized and examined as a cathode for the intermediate temperature (400 to 650 °C) applications. ITSOFCs using this cost-effective perovskite as a cathode displayed an excellent cell performance: between 300 and 1500 mA cm^{-2} (100 to 500 mW cm^{-2}) for temperatures ranging from 450 to 600 °C. The role of AgO as additive to the perovskite has also showed an enhancement in the fuel cell performance.

Keywords: Intermediate temperature SOFCs, ceria-composites, perovskite, oxygen ion conduction, CLM (Ca_{0.9}La_{0.1}MnO_3)

La_{0.6}Ca_{0.4}CoO_3, La_{0.1}Ca_{0.9}MnO_3 and LaNiO_3 as Bifunctional oxygen electrodes

M. Bursell, M. Pirjamali, Y. Kiros *

Department of Chemical Engineering and Technology, Chemical Reaction Engineering, Royal Institute of Technology (KTH ), S- 100 44 Stockholm, Sweden

Abstract
A series of perovskite catalysts was investigated for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in alkaline electrolyte and at room temperature, supplied by oxygen or air. A meniscus cell was used to screen-test candidate catalysts for their bifunctionality and assess their activity.
for ORR at 3 mm depth of immersion (DOI) in the electrolyte. Based on the meniscus data LaNiO₃, La₀.₁Ca₀.₉MnO₃ and La₀.₆Ca₀.₄CoO₃ were selected for further assessment in microelectrode and half-cell studies. Activity tests for the ORR and OER, Tafel slopes at high current densities and apparent activation energies for the ORR were determined using a microelectrode technique on samples of the selected perovskites, La₀.₁Ca₀.₉MnO₃, La₀.₆Ca₀.₄CoO₃ and LaNiO₃ with and without graphite support. Tafel slopes of ca. 120 mV per decade and apparent activation energies of approximately 18 kcal mol⁻¹ were measured at high cathodic current densities. Cycle-life and performance of La₀.₁Ca₀.₉MnO₃, La₀.₆Ca₀.₄CoO₃ and LaNiO₃-based gas-diffusion electrodes in half-cell configurations were tested at a constant current density of 25 mA cm⁻² with subsequent and intermittent polarizations. Similar activities resulted in the ORR, while increased numbers of cycles were observed for the La₀.₁Ca₀.₉MnO₃-based electrode. Furthermore, electrode material compositions, especially PTFE contents were optimized to conform to the establishment of the three phase interactions of the electrode structure. Transmission Electron microscopy (TEM) and BET-surface area analyses were carried out in order to find out the morphological and surface properties of the perovskite materials.

Keywords: Bifunctional electrode; Perovskite; Microelectrode; Gas-diffusion electrode; Stability; Activity


Effect and characterization of dopants to Raney nickel for hydrogen oxidation

Y. Kiros a*, M. Majari a, T.A. Nissinen b

a Department of Chemical Engineering and Technology, Chemical Reaction Engineering, KTH-Royal Institute of Technology, S-100 44 Stockholm, Sweden
b Laboratory of Materials Processing and Powder Metallurgy, Helsinki University of Technology, P.O. Box 6200, FIN-02015 HUT, Finland

Abstract

Raney nickel and its alloys with the transition metals were prepared and investigated as gas diffusion electrodes for the hydrogen oxidation reaction (HOR) in 6 M KOH and at 60 °C. The spongy Raney nickel prepared by a mixture of Ni and Al with a weight ratio of 1:1 was compared for the catalytic activity as hydrogen electrodes with other alloy formations containing 2 wt.% of Cu, Fe, Cr, Ti and La. Depending on the composition of the active layer, the electrocatalytic activity of the Raney nickel was found to decrease in a descending order of the doped metals: Cr > La > Ti > Cu > Fe and with no admixture. The catalytic response of the electrodes, especially for the Cr and Ti-based Raney Ni showed high enrichment and aggregation on the surface and hence affects the activity and stability. Surface area, particle size, average pore diameter, particle morphology and surface elements of the various alloy combinations, have been analyzed and assessed using BET-specific surface areas, SEM and EDXS.

Keywords: Transition metal alloys; Catalysis; Electrochemical reactions; Microstructure; SEM

Catalyst spinel MnCo$_2$O$_4$ with particle size <30 nm was prepared by a novel microwave-assisted route. To determine the optimal amount of carbon needed as a microwave susceptor, varying amounts of amorphous carbon powder (7-26 wt %) were mixed with the aqueous solutions of Mn- and Co-nitrates. After heat treatment at 200 °C in a conventional oven, the mixtures were heat-treated in a microwave oven (2.45 GHz) at a power of 350 W. The effect of the carbon amount on the formation and properties of the catalysts was studied. In this production method, 13 wt % of carbon was found to be the minimum needed for spinel MnCo$_2$O$_4$ formation. Most of the carbon was oxidized during the microwave treatment. When the carbon content in the nitrate-carbon mixture was increased beyond 13 wt %, the carbon content and the specific surface area of the final catalyst started to decrease. However, the carbon amount of 18 wt % in the initial nitrate-carbon mixture was found to be the most preferable when considering the catalytic activity of the spinel toward oxygen reduction reaction in alkaline electrolyte.
Comparison of preparation routes of spinel catalyst for alkaline fuel cells

Terhi Nissinen*a, Yohannes Kirosb, Michael Gasika, Markku Lampinen.c

aHelsinki University of Technology, Laboratory of Materials Processing and Powder Metallurgy, P.O. Box 6200, FIN-02015 HUT, Finland
bRoyal Institute of Technology (KTH), Department of Chemical Engineering and Technology, Chemical Reaction Engineering, S-100 44 Stockholm, Sweden
cLaboratory of Applied Thermodynamics, P.O. Box 4400, FIN-02015 HUT, Finland

Abstract
MnCo2O4 has been used as a catalyst for oxygen reduction reaction (ORR) in alkaline fuel cells due to easier production and lower costs compared to noble metals. A novel method using a microwave-assisted route of synthesis in the presence of amorphous carbon was developed resulting in MnCo2O4 with particle sizes <30 nm. For comparison, spinel prepared in a conventional oven with or without carbon was also studied. The surface area, carbon content, and chemical and morphological properties of the catalyst materials were analyzed. The catalytic activity towards oxygen reduction reaction was measured in a half-cell in 6 M KOH and by microagglomerate method. Compared to the catalysts prepared in a conventional oven, microwave-assisted route resulted in higher specific surface areas, higher current densities and stability, as well as lower apparent activation energies and Tafel slopes.

Keywords: A. Oxides; A. Nanostructures; B. Chemical synthesis; C. Electrochemical measurements; D. Catalytic properties


Zr-Based AB2-Type Hydrogen Storage Alloys as Dual Catalysts of Gas-Diffusion Electrodes in an Alkaline Fuel Cell
Wei-Kang Hu,† Xue-Ping Gao,*‡ Yohannes Kiros,§ Erik Middelman, and Dag Noreus*,†
Department of Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden, Institute of New Energy Material Chemistry, Nankai University, Tianjin 300071, China, Department of Chemical Engineering and Technology, Chemical Reaction Engineering, KTH-Royal Institute of Technology, S-100 44, Stockholm, Sweden, and NedStack Fuel Cell Technology BV, Arnhem, The Netherlands

Zr-based AB2-type hydrogen storage alloys as dual catalysts for hydrogen adsorption and oxidation reactions in alkaline fuel cells were investigated. A hydrogen-diffusion electrode composed of this hydride alloy was constructed, and its performance in terms of catalytic activities and durability was evaluated. Results demonstrated that the hydrogen-diffusion electrode had not only good activity but also excellent stability at a current density of 40-60 mA/cm2 after surface treatments using a 1.0 M HF solution. XPS analyses showed that the improvement in catalytic activity is related to the formation of a nickel-rich layer and the removal of other oxides on the catalyst surface. The novel possible application of Zr-based hydride alloys could lead to an attempt to exploit new catalysts to lower material cost for hydrogen fuel cells.


Wei-Kang Hu,† Yohannes Kiros,‡ and Dag Noreus*,†
Department of Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden, and Department of Chemical Engineering and Technology, Chemical Reaction Engineering, KTH-Royal Institute of Technology, S-100 44, Stockholm, Sweden

Development of a non-noble-metal catalyst electrode is an important issue in the research and development of fuel cells. The catalytic activity and durability of AB5-type hydrogen storage alloys used in hydrogen
diffusion electrodes for alkaline fuel cells are evaluated. The experiments demonstrate that the activity and stability for hydrogen oxidation is greatly improved if the particle size is decreased from 5-30 to 1-10 µm. This also improves the electrode stability. SEM and XRD analyses show that no disintegration of the smaller catalyst particles is observed in long-term tests. A novel H₂/hydride/perovskite/O₂ alkaline fuel cell was constructed as a non-noble-metal fuel cell concept. The results showed that both gas-diffusion electrodes had high catalytic activities and good stability. A maximum power density of 54 mW/cm² was achieved at 120 mA/cm² when using H₂/O₂ and 49 mW/cm² at 100 mA/cm² when using H₂/air.


Oxygen reduction electrodes for electrolysis in chlor-alkali cells
Yohannes Kiros *, Massoud Pirjamali, Martin Bursell
Department of Chemical Engineering and Technology, Chemical Reaction Engineering, Royal Institute of Technology-KTH, 100 44 Stockholm, Sweden

Abstract
Oxygen reduction electrodes, containing non-noble metal catalysts supported on high surface area carbon and wet-proofed with PTFE were tested under reaction conditions for the chlor-alkali electrolysis. Double-layer gas diffusion electrodes were prepared by rolling of an active layer and diffusion layer on a nickel wire screen, compressed and sintered at 300 °C. Electrochemical measurements for substantiating the activity and stability of the half-cells were conducted in 8M NaOH by supplying oxygen at a cell temperature of 70 °C and a constant current load of 300 mA cm⁻². An electrolysis cell with a dimensionally stable anode (DSA) and double-layered cathode was assembled, where 4.8M NaCl and oxygen were supplied, respectively for the production of chlorine and NaOH. The cell performances as well as stability of the electrodes were investigated at about 80 °C. This study shows that by replacing the high voltage consuming hydrogen-evolving reaction and by adopting highly active electrocatalysts as cathode materials, energy savings of more than 30% could be realized.

Keywords: Oxygen reduction, cathode, Non-noble metal electrocatalyst, Activity, Stability, Chlor-alkali electrolysis


Metal porphyrins for oxygen reduction in PEMFC

Yohannes Kiros
Department of Chemical Engineering and Technology, Chemical Reaction Engineering, Royal Institute of Technology (KTH), 100 44 Stockholm, Sweden

Abstract
A short literature review on alternative catalysts for the cathodic oxygen reduction in acid (H₂SO₄) and polymer electrolyte membrane fuel cell (PEMFC) with special emphasis on pyrolyzed macrocycles and precursor materials from metals, organic molecules and N-containing elements has been conducted. Furthermore, various catalytic materials comprising two different concentrations of iron and cobalt tetramethoxyphenyl porphyrins and perovskites were prepared by both the impregnation and precipitation reactions. Screening tests of the individual catalytic materials and their mixtures were carried out in half-cell measurements using the rotating disc electrode (RDE) in 0.5M H₂SO₄ and at room temperature. Cyclic voltammograms were recorded at a scan rate of 10 mV s⁻¹ both with and without rotations. The peak potential at 0 rpm was used to study and compare the catalytic activities towards oxygen reduction reaction
Concentrations of 30wt% Fe and Co/TMPP have shown increased performance characteristics, while those with lower or increased contents, acid-treated and mixed with perovskite have displayed lower activities. Polarization data for the catalyst containing 30wt% FeTMPP was also obtained. Acid leaching of the pyrolysis products has resulted in substantial decrease of the metals from the pyrolysis products supported on carbon. TEM, BET-surface area and EDX analyses on the samples have shown high aggregation of the metals with crystalline structure, surface areas depending on the compositions of the catalysts and increased surface concentration of the metals with absence of nitrogen on the moiety.

Keywords: Oxygen reduction; Metal porphyrin; RDE; PEMFC; TEM, BET-surface; EDX

Low energy consumption in chlor-alkali cells using oxygen reduction electrodes

Yohannes Kiros, Martin Bursell

An air/oxygen gas diffusion electrode for use as a cathode to replace the traditional hydrogen-evolving electrode in chlor-alkali electrolysis was assessed. Attempts to stabilize the cathode have been addressed in order to circumscribe problems associated with “flooding” or “wetting-in” properties. Variation of the hydrophobic concentration in the gas diffusion layer had a significant effect on the electrochemical tests of both the half-cell and electrolysis of the chlor-alkali cells. Life-tests as well as performance characteristics for both types of cells have shown encouraging results at NaOH concentration levels of ca. 8M NaOH and temperatures of 70 and ca. 80 °C, respectively. Though cell voltages of about 2V were achieved and thereby reducing the energy consumption by 30-35% compared to the state-of-the-art membrane cell, the contributions of overvoltages were still high compared to the equilibrium potential of about 1.23V. Efforts to limit the individual parts of overvoltages as well as maintenance of the zero-gap cell at least on the anode side have been carried out. Two different kinds of cation exchange membranes have been used for the electrolysis cell. However, the cation exchange membrane with hydrophilic properties having high initial performances showed tendencies of blister formations.

Keywords: chlor-alkali; electrolysis; oxygen reduction; energy consumption; overpotentials