Alkaline Membrane Fuel Cell Workshop Final Report

Workshop held December 11-13, 2006

Embassy Suites Hotel-Phoenix Airport, Phoenix, AZ, USA

Sponsored by

Army Research Office (ARO)

Principal Investigator
Bryan Pivovar
Fuel Cell Team Leader
Los Alamos National Laboratory
PO Box 1663, MS D429
Los Alamos, NM 87545

Organizing Committee
Peter Fedkiw, North Carolina State University/ARO
Robert Mantz, ARO
Bryan Pivovar, Los Alamos National Laboratory

Break-out Group Chairs
Thomas Zawodzinski, Case Western Reserve University
James Boncella, Los Alamos National Laboratory
Robert Slade, University of Surrey
Andrzej Wieckowski, University of Illinois – UC
Sanjeev Mukerjee, Northeastern University
Deryn Chu, Army Research Laboratory
Paul Kenis, University of Illinois – UC

Table of Contents

Executive Summary

The findings of individual breakout groups from the Alkaline Membrane Fuel Cell Workshop are reported in the following sections. The Executive Summary, given here, is meant to highlight specific aspects of the workshop and report on general consensus (and dissent) of the joint session. Summaries of the key recommendations of the breakout groups can be found at the end of the Executive Summary in Table 1.

Alkaline fuel cells have the potential to offer significant performance advantages over batteries or traditional (acidic) polymer electrolyte membrane (PEM) fuel cells at low power levels. Fuel cells, in general, have distinct advantages over batteries because they use high energy density fuels. Alkaline membrane fuel cells offer significant advantages over traditional (aqueous KOH-based) alkaline fuel cells, in that membrane based systems avoid issues of electrolyte migration, mitigate corrosion concerns, can be operated with differential pressures, prevent carbonate precipitation and offer design simplification. The primary advantages of alkaline membrane fuel cells compared to traditional PEM fuel cells center on increased materials stability at high pH (allowing for non-precious catalysis), increased electrocatalytic activity in alkaline conditions (particularly for organic fuels such as methanol or ethanol), increased fuel choices in basic environments (ammonia, borohydride), and decreased fuel crossover rates/potentially improved water management (arising from electro-osmotic drag and the flux of hydroxide ions in the opposite direction of protons in traditional PEM fuel cells).

The most critical shortcomings of alkaline membrane fuel cells are their relatively poor stability and the low conductivity of currently available alkaline membranes. The poor stability of these membranes has limited the lifetimes of demonstrated devices (to a few days) and required low temperature operation (less than 60˚C) in order to achieve even these limited lifetimes. The low conductivity of these membranes is in part due to the decreased mobility of hydroxide ions versus protons. The use of alkaline membrane fuel cells also creates concerns regarding carbonate formation and carbonate/hydroxide equilibria that are not well understood but likely lead to performance loss. Alkaline membranes have not yet been demonstrated as high performance membrane electrode assemblies (MEAs) without the addition of free electrolyte. Finally, alkaline membranes have shown much greater dependence on water content than PEMs, making water management in these systems even more critical (while this statement may seem to contradict the potentially improved water management of these systems, there is a distinction here between the retention of water of these systems (advantage from a fuel energy density or water recovery standpoint) and the increased dependence of performance and durability on dehydration of these materials).

While the aforementioned shortcomings or concerns exist regarding alkaline membrane fuel cells, recent advances suggest that some of these shortcomings may either be less of an issue or that there may be engineering or advanced material solutions that may enable the technology. For example, non-precious catalysts have been reported (by ACTA) to produce complete electrochemical conversion of alcohols (methanol and ethanol) and low overpotentials. Cells fabricated on such technology have shown power densities more than sufficient for low power devices, > 90 mW/cm^2. Preliminary efforts at producing membrane electrode assemblies has resulted in cells with relatively stable performance over days, suggesting adequate chemical stability can at least be achieved for some short lifetime applications, although the lifetime limits of these systems remain an area of much research need. Finally, limitations due to carbonate formation have been called into question as performance degradation due to this phenomenon has not been found in lifetime experiments to the same extent as had been reported in early alkaline (free electrolyte) fuel cells. Because of these advances, the general consensus of the Workshop's participants was that alkaline membrane fuel cells both require and merit further research, and that *research funding at this point in time has a high probability of resulting in systems that can deliver improved performance* at a likely lower cost.

There was agreement that research should be focused on devices in the 20-100 W level due to perceived military needs and conductivity limitations for higher power devices. Lower power levels (and passive devices, in the 1-5 W range) were also intriguing due to the possibility of water neutral operation, but were not discussed to the same extent due to limited military application, although such devices are of interest for commercial portable electronics.

Consensus within the Joint Session about the highest need for this technology was not achieved, with personal opinion generally in line with a specific researcher's area of expertise. The debate over the importance of topical areas roughly broke down along the lines of the breakout groups with Electrocatalysis, Membranes/Cations, or Utilization in Fuel Cells being the primary concerns. A general consensus appeared to be reached, in that System Issues (the final breakout group) was an important aspect of each of these areas.

While debate amongst the importance of the different research areas existed, there was a general consensus within each topic area as to what the most important needs were, and also, what the factors in determining priority between different research areas would be. The findings of the breakout session are given in more detail in the body of this report, while the top research topics and issues associated with these topics are presented here, briefly.

The need for improved membranes in alkaline membrane fuel cells was widely recognized. While the current membranes may suffice for low temperature, limited lifetime operation, improvements in conductivity and durability would enable many applications and improve performance in others. Materials development efforts are necessary to produce next generation membranes materials with increased durability and improved conductivity.

While improved electrocatalysis is an agreed upon advantage of an alkaline system, specifics about catalytic performance and catalysts capable of efficiently oxidizing more complex molecules are of great interest. These catalysts could potentially be used in membraneless devices as well, reducing the need for advanced membranes. Improved catalysts could allow for ethanol or other fuels that have advantages due to energy density, availability, or safety concerns to be used. Materials development efforts are necessary to study novel electrocatalysts, particularly as they apply to alternative fuels (fuels beyond hydrogen, methanol and formic acid).

While ACTA has claimed direct (and complete) electrochemical oxidation of ethanol at relatively low overpotentials, the ability to produce high performance MEAs without added electrolyte has not been demonstrated. The challenges associated with creating electrodes and employing membranes and catalysts in systems is another critical aspect of employing alkaline membrane technology. Advanced electrode architectures that avoid the use of free electrolytes and their impact on performance need to be investigated.

Finally, the importance of each of these issues depends on the system and application, and it will be important to have system integrators advising researchers on the tradeoffs and benefits of materials improvements.

Table 1: Key Recommendations of Breakout Groups

Breakout Group	Key Recommmendations
Anion Exchange Membrane/Cation Stability and Conductivity	**Improve cation stability** – current generation materials have had significant limitations due to chemical stability of the cations, explore different classes and novel cations, explore degradation mechanisms and dependence on temperature and water content. **Improve conductivity –** conductivity in these systems is significantly lower than in acid membrane systems, the role of cation basicity, water content and membrane morphology need to be related to conductivity and carbonate formation needs further investigation.
Electrocatalysis in High pH Environments	**Catalysts for complex fuel oxidation –** the ability of alkaline systems to effectively utilize complex fuels like ethanol is a significant advantage over related systems, how they do this and whether or not they can be effectively expanded to include more complex fuels (like gasoline) is an area that needs further investigation.
Utilizing Anion Exchange Membranes in Fuel Cells	**MEA fabrication –** current generation cells only obtain system useful performance with the addition of free electrolyte, research to improve performance of cells without free electrolyte are required for many applications.
System Considerations/Needs	**System Issues** - will depend on system specific requirements, but work in this area is necessary to determine how much improvement is needed in each of the other areas to produce viable devices.

Introduction

DoD has significant needs for improved power sources in mW to kW devices. In recent years, polymer electrolyte fuel cells have been intensely investigated due to their potential for displacing competing technologies, particularly batteries in low power applications.[1,2] Traditional polymer electrolyte fuel cells operate with a proton conducting membrane and have several limitations associated with water management, electro-catalysis and materials stability, for example.[3,4] Alkaline (basic or anion exchange) membrane based fuel cell systems have shown the potential to overcome many of these limitations.[5]

Alkaline membranes have only within the past few years garnered significant attention from the research community. Only a small amount of research on these systems and materials appears in the literature, and an attempt to quantify the state of the art, and establish limitations, performance potential and research needs of alkaline membrane fuel cell systems has not been attempted prior to this workshop

Workshop Objectives and Organization

The objectives of this Workshop were to: 1) assess the state of alkaline membrane fuel cell technology; 2) identify the limitations of alkaline membrane fuel cell technology; 3) establish performance potential of alkaline membrane fuel cell systems; and 4) establish and prioritize research needs for these systems.

The Workshop was held at the Embassy Suites – Phoenix Airport 44th St in Phoenix, AZ from December 11-13, 2006. A group of 62 participants including national and international experts in the areas of fuel cells, polymer electrolytes, electrocatalysts, and power systems participated. These participants represented industry, academia, national laboratories and the military. The workshop format was similar to past successful ARO workshops. The workshop opened with an overview of military power source needs and an overview of alkaline membrane fuel cells on Monday evening (Dec. 11). Tuesday morning (Dec. 12) a series of invited talks on more targeted areas of concern for the development of alkaline membrane fuel cells systems were presented.

Breakout groups met Tuesday afternoon (Dec. 12) and Wednesday morning (Dec. 13) to discuss four specific topical areas: 1) Anion Exchange Membrane/Cation Stability and Conductivity; 2) Electrocatalysis in High pH Environments; 3) Utilizing Anion Exchange Membranes in Fuel Cells; and 4) System Considerations/Needs. Each one of these sessions had a Chair or co-Chairs in order to facilitate discussion and capture the discussion. Following the Breakout Sessions, a Joint Session was reconvened where the Chair of each Breakout Session presented their findings. These findings were then briefly discussed within the Joint Session.

The workshop agenda, a list of workshop participants, and all of the workshop presentations, including the findings from the Breakout groups, can be found on the CD distributed to all the attendees and serves as an Appendix to this report.

Breakout Session Findings

The majority of discussion at the workshop, including review of the invited presentations, occurred in the Breakout Sessions. The four Breakout Session topics along with suggested topical issues are found below (session Chairs given in parenthesis).

- **Anion Exchange Membrane/Cation Stability and Conductivity** (James Boncella and Thomas Zawodzinski)
    - Chemical stability of cations and backbones
    - Alternative chemistries
    - Effect on stability and conductivity
- **Electrocatalysis in High pH Environments** (Andrzej Wieckowski and Sanjeev Mukerjee)
    - Oxygen reduction
    - Anode electrochemistry
    - Alternative fuel electrochemical activity (C-C bonds)
    - Catalyst durability
- **Utilizing Anion Exchange Membranes in Fuel Cells** (Robert Slade)
    - Membrane electrode assembly fabrication
    - Catalyst utilization
    - Effects of added free electrolytes
    - Fuel cell performance
- **System Considerations/Needs (**Deryn Chu and Paul Kenis)
    - Power/Energy density
    - Active versus passive systems
    - Effect of operating conditions
    - Balance of Plant Issues

The findings of the breakout sessions relative to the workshop goals are presented below. Additionally, the presentations from each of the breakout groups can be found on the accompanying CD. As the topical areas are not completely independent, each one of the following sections has some crossover with other sections. A summary of the findings and recommendations can be found in the executive summary. The following sections have been prepared by the respective session Chairs plus the Principal Investigator (in the case of the Utilizing Anion Exchange Membranes in Fuel Cells section) with only minor editing (by the Principal Investigator of the other sections).

Anion Exchange Membrane/Cation Stability and Conductivity

<u>State of the Art</u>: Alkaline fuel cells (AFCs) have been made for many years. Aqueous potassium hydroxide (KOH) has been the primary choice of electrolyte, but substantial research has also been carried out on carbonate/bicarbonate electrolytes as well. These have been used in contained and flowing systems. Practical devices are used in space applications, with highly evolved solutions to stability and corrosion problems. etc.

For terrestrial applications, it is likely that a more compact system will emerge from the use of membrane systems, and these will be the primary focus of this discussion. However, we do not believe that it is wise to categorically eliminate options for flowing or recirculating systems. In particular, recent advances in ‘membrane-less’ or laminar flow fuel cells may present a viable option.

It is also important to note that there are a few currently available hydroxide-conducting membranes that are commercially available. However, systems employing these materials (have been developed for other applications and) are currently limited in terms of performance and durability. Most alkaline membrane fuel cells that have been demonstrated have been limited to low temperatures (below 60˚C) and still have not demonstrated long lifetimes (few days).[6]

The underlying mobility of the hydroxide ion is somewhat faster than most other ions due to its access to Grotthus-type H-atom exchange processes. However, OH^- mobility is inherently slower than that of protons (infinite dilution diffusion coefficients suggest a factor of 2 decrease in conductivity, but membrane conductivity data such as that given in the workshop presentation of Slade suggest a factor of 3 to 5). Thus, there is an initial concern regarding the achievable conductivity relative to proton conducting systems. A possible resolution of this concern lies in the realization that the conductance of the membrane will be the determining factor in any device and present-day electrolyte thicknesses as well as relatively low current density at high efficiency operation points are needed. Thus, IR loss may not be a large factor, but this will also limit these systems to relatively lower power densities.

Limitations and Concerns: Several limitations and concerns of existing or projected technologies must be considered. The salient questions regarding these electrolytes arise from a few unique aspects relative to the corresponding acid systems. These are:

- An overriding concern is the stability of the cation in the presence of strong base
- The need to deal with equilibria amongst OH^-, carbonate and bicarbonate anions, especially in the context of carbonaceous fuel sources
- The lower conductivity of basic electrolytes relative to their more familiar protonic counterparts not just in the membrane but in the electrodes.

There are several specific concerns regarding the stability of the cations.[7,8,9,10,11] The most common type of cationic moiety used in anion conducting membranes is a quaternized nitrogen atom, but these functional groups are susceptible to attack by hydroxide via several mechanisms that ultimately destroy the cation.[12] The hydration state of the hydroxide ion greatly affects its reactivity as both a base and a nucleophile, with the reactivity greatly increasing as the ion is dehydrated. *Strategies to increase cation stability by maintaining solvation have the potential to have negative impacts on various aspects of the overall fuel cell design. Indeed, this may be the single most important focal point for membrane research.*

Some more specific recommendations for how to increase cation stability include:

- Building bulky cations

- Cations containing macrocyclic ligand complexes of metals
- Cations in which nitrogen does not carry the positive charge
- Putting hydrophilic moieties around the cation to solvate hydroxide under low relative humidity conditions
- Eliminate beta H's

An additional concern for the membrane work is the interaction of the membrane with specific fuels. In particular, we want to consider whether certain fuels are ruled out because of negative impact on membrane or electrode materials.

Possible Approaches: The use of cations that have more specialized structures than the typical quaternary ammonium ions is worth investigating. The synthesis of cations that are inherently less susceptible to deprotonation or attack by hydroxide may be possible and could solve the issues related to cation stability.[13] Some strategies worth pursuing in this regard are:

- Development of systems with local H-bonding opportunities to solvate the OH^- and facilitate its departure from the cation site
- Continued exploration of means of stabilizing cation sites relative to base attack using steric hindrance or appropriate modification of electron density
- One concern is the need to avoid overly bulky cationic sites which lower the ionic content and, potentially, create too much space between adjacent sites

Virtually nothing is known about the fate of carbonate or bicarbonate arising from the reaction of CO_2 with hydroxide in the membrane. An understanding of the rate and thermodynamics of partitioning of these species in the membrane and whether or not they will precipitate in the membrane will be crucial to developing robust systems that can utilize carbonaceous fuels such as methanol, ethanol or other hydrocarbons.

There is a definite need for a well-articulated program of characterization of key properties of the electrolytes. These include durability assessment as well as physical characteristics derived from water uptake and transport measurements, mechanical characterization and thermochemical studies that have been extensively deployed in acid systems. There is a perceived need for a testing protocol that represents a 'low bar' for initial screening, followed by successively more stringent challenges. We recommend such a procedure because we want to be inclusive at early stages but provide 'constructive criticism' to drive iteration on electrolyte chemistry and properties. This characterization must simultaneously meet the needs of systems analysis (providing data for evaluation of new electrolytes in a system framework), system construction and operational concerns as well as the choices of material (What classes of backbone polymers should be avoided because of stability concerns?).

Electrolyte-electrode interactions are an important component that must be integrated into development of new electrolyte chemistry.[14] A critical factor is the design of composite electrodes. The understanding of composite electrode transport is important in this context but is addressed by the MEA portion of the report. Of relevance here are:

- Avoid cation adsorption

- Ensuring that materials can be processed to provide good electrode structures and good electrolyte/electrode adhesion
- Assessing the impact of peroxide production on stability
- Understanding the influence on catalysis of various materials in the region near the catalyst particle.

Some possible approaches to solve the problems associated with the conductivity of these types of systems include the use of block co-polymers to give phase-separated systems that will facilitate hydroxide conduction. In a well-separated system, the possibility for conduction that takes advantage of a hoping type mechanism exists and should be investigated.[15] Other options include the use of gelled and composite systems.[16] An important fundamental concern that should be pursued is the rapid decline in conductivity of OH^- conductors with decreasing RH. Insight from theory could pay substantial dividends in this regard. This is especially true in the context of understanding conductivity in electrolyte morphologies—e.g. block copolymers—that contain water in confined regions within the polymer. In short, how does the nature of H-bonding networks that arise in these systems influence the conduction process?

Some consideration, as a lower priority, should be afforded to solid electrolytes and glasses. We are uncertain about the availability of fast ion conductors of the glass or solid electrolyte type that can provide appropriate levels of conductivity at low or moderate temperature. The priority is lowered because of perceived difficulty of attaching electrodes to these types of electrolytes. In short, the materials could have drawbacks of both high T and low T conductors, with the low catalysis and transport rate associated with low T coupled to the limited triple-phase interface associated with high T electrolytes.

R&D Needs: In the area of cation/membrane stability the following are recommendations for research needs:

Higher Priority

- Maximum range of new electrolyte concepts: several years of free range for synthesis; focal points should be:
    - Cation stability and basicity (chemistry and the effects of hydration)
    - Polymeric membrane systems that are probably the most promising
- In parallel, investigate capabilities from presently available materials
- Understanding of carbonate/bicarbonate/hydroxide chemistry
- Strong characterization and fundamental theory effort
    - Factors favoring highest conductivity
    - Durability
- Strong connection to system questions
    - Conditions for evaluation, targets evolve from system concepts
    - Assessment of system viability and possible application spaces for lower priority electrolyte systems
- Also connect strongly to electrode issues: coating of membrane, development of electrode structure

Lower Priority

- Development of polymer ‘platforms’ for rapid screening of cation and cation tether stability
- Assessment of fuel options based on membrane/fuel compatibility and permeation
- Liquid electrolytes
- Circulating electrolytes
- Gel electrolytes
- Solid or glassy electrolytes

Electrocatalysis in High pH Environments

State of the Art: Alkaline fuel cells offer a series of advantages associated with enhanced electrocatalytic activity, as well as the ability to use non-noble metal electrocatalysts.[17] The principal reason for operating a fuel cell in a high pH environment is that this affords greater fuel flexibility due to the possibility to oxidize at low temperature fuels beyond hydrogen, formic acid and methanol.[18] Thus, the potential benefits of alkaline systems in terms of choice of materials, operating conditions, and fuel input have to be defined in comparison to competing PEMFCs. The key challenge lies in fundamental understanding of oxidation reactions of fuels with a carbon-carbon bond, and practical demonstration of integration of such electrocatalysts with the newly developed alkaline polymer membranes (anion exchange membranes).

There is a substantial record of using non-noble metals (or metals like Ag or Ni) in alkaline fuel cells or technologically related systems (metal air batteries).[17, 19] For the most part, however, these uses were limited to relatively low current densities and practically all of them were explored in liquid electrolyte (KOH or NaOH) only. Most of the current state of the art in practical high-power alkaline fuel cells is still predicated on (i) the use of noble metals relying perhaps on the controversial claim of lower overpotential losses for oxygen reduction on Pt. (ii) Better ability to oxidize alcohols affording fuel flexibility. (iii) Wider choice of stable catalytic materials, including non noble metals which can approach the activity of Pt for cathode application.[20]

Of particular interest are results reported at the workshop by Acta (see presentations) in which alkaline membrane fuel cells have been run using ethanol (with reported complete electro-oxidation of the ethanol molecule), ethylene glycol or even gasoline (without reported complete oxidation). The reported fuel cell performance using ethanol shows relatively low anode overpotentials and high performance. The use of any of these high energy density fuels containing carbon-carbon bonds demonstrates the promise of these types of systems.

Limitations and Concerns: The practice of applying catalysts to fuels with a carbon-carbon bond (such as ethanol) and integration of such catalyst into anion exchange membranes is rather limited. Electrocatalysis of methanol electro-oxidation and even more, ethanol electro-oxidation have not been studied in detail, and thus present a challenge to practical implementation. A limitation has been the interfacial mass transport losses, due to carbonate formation over time. However, the principal gaps include (a) Lack of clear understanding of C-C bond scission at the anode. (b) Many choices for the anode electrocatalysts have been suggested, however the overwhelming prior work centers on direct methanol anodes. (c) There is very good evidence on the ability of organic macrocycles,[21] base metals such as Ag,[20] and metal oxides[22] being able to meet and in some claims exceed the ORR performance of Pt. However, sufficient knowledge of the electrocatalysis (active reaction center) and proper systematic comparison of activity is unavailable. (d) Systematic studies in multitude of electrolytes and complex fuels are not known. (e) No systematic knowledge of durability, electrolyte poisoning etc., exists.

Possible Approaches: Approaches and opportunities for investigating both the anode catalysts and cathode catalysts exist.

Anode Electrocatalysts:

- Investigation of the mechanism of electro-oxidation of methanol, ethanol and glycerol in alkaline media towards revealing the mechanism of the catalysis and identifying the rate-limiting steps.
- “Catalyst-by-design” approach for new generation of anode catalysts synthesis based on the understanding of the mechanism and engineering the surface to address bi-functional or mediated (cascade-type) electro-oxidation of ethanol.
- Engineering of anode catalysts material by creating surface architectures that present the active sites linked to the mechanistic steps to the specific transport properties of a water-generating anode.
- Selection of non noble metal electrocatalysts able to oxidize complex fuels starting with ethanol. Ability to handle C-C bonds effectively with low overpotential losses. This is key for fuel flexibility. Here novel approach to exploit surface mediated processes with tandem reactions on different complimentary reaction centers instead of a more conventional bifunctional approach.
- Cheaper materials choices and adapting the material set to accommodate alkaline environment and the alternative water management issues.
- Choice of support materials for affording better durability, catalyst compatibility with ionomer and membrane, and exploiting metal-support interactions. Developing of active supports or “self-supported” electrocatalysts that will provide both electrical connectivity and catalytic functionality.
- Compared to PEMFCs, wider choice of anode materials affords better ability to choose appropriate electrolyte environment.

Cathode Electrocatalysts:

- Choice of depolarized cathode electrocatalysts which can tolerate significant fuel crossover.
- Non-noble metal systems enabling cheaper, more durable reaction centers.

- Use of organic macrocycles theoretically enables significant lowering of cathode overpotential.
- Greater compatibility with wide variety of alkaline electrolytes.
- Design of catalysts and/or catalyst supports that should retain humidity in a “drying” cathode environment. Design for a passive cathode with a “build-in” water management.

R&D Needs: In the area of electrocatalysis at high pH the following are recommendations for research needs:

(1) Non-noble metal catalysts for complex fuel oxidation, especially for ethanol.

- Novel synthesis of well-defined non-noble metal structures for complex fuel oxidation.
- Understanding competing pathways for oxidation of complex fuels.
- Overcoming critical barriers in electrocatalysis via cascade or mediated design of electrodes or mixed catalyst systems.

(2) Understanding ORR in mixed feed environments

- Designing cathode electrocatalysts with ability to handle oxygen reduction in mixed fuel-oxidant environments.
- Much is already known from early work on catalysts for alkaline fuel cells, but this needs to be updated with attention to recent advances in PEMFC electrocatalysts. For instance, the use of core-shell approaches to achieve higher activity,[23] and modification of d-band center as a major parameter in determining electrode kinetics.[24]

(3) The synthetic work of catalysts

- Understanding the effect of novel synthetic approaches for mixed transition metal oxides, base metal analogs and macrocycles.
- Determining critical support interactions for improved compatibility.

(4) Work by the new methods to describe the catalysis better.

- Effective use of new *in situ* tools. Examples: SFG, Synchrotron *in situ* Methods using X-ray Absorption {Delta Mu Technique}, Electron Microscopy, *in situ* EPR.
- On-Line Product Detection for determination of selectivity / reaction pathways.
- Mechanistic Issues – examination using electrochemical measurements, impedance, etc.
- Kinetic modeling of reaction pathways in conjunction with steady-state measurements.
- Transport (mass transfer in the three phase zone as well as the electrolyte). Optimization of three-phase interface may be needed to overcome lower O_2 permeability.
- Charge Transfer Kinetics – further work needed to understand/optimize electrocatalytic activity at both electrodes

- Decay-rate (Catalyst, Ionomer and Membrane) – Some alkaline ORR catalysts (e.g. Pt and Ag) show better stability under alkaline oxidizing conditions than equivalent materials in acidic fuel cells, but long-term electrode stability, including interfaces between catalyst/support and electrode/membrane, are unknown.
- Screening Methods {Real Life}. Catalytic studies should be performed as much as possible under fuel cell relevant conditions. Attention should be given to appropriate selection of electrolyte – carbonate / hydroxide concentration, and possible use of dissolved anion exchange membrane monomers as model fuel cell electrolytes.

(5) Electrocatalyst-Electrolyte Interface [adjust catalysts to the type of fuel (starting with ethanol), membrane and electrolyte].

- Utilization (Fuel, Catalyst etc.) – much work has gone into optimization of PEMFC MEAs to ensure high utilization of catalyst.[25] Anion-exchange FCs face additional problems associated with the poor interface between membrane and electrocatalyst. Use of interfacial polymers needs to be investigated to ensure high catalyst utilization.
- Ink formulations and eventual incorporation into reaction layers with a variety of membranes.
- Understanding Operating Variables: Temperature, Pressure, Overpotential, pH etc. These are well-known for certain model catalysts (e.g. Pt), but less known for non-noble catalytic materials. Appropriate selection of operating conditions, with respect to membrane/system considerations and specific needs of each individual catalyst, will yield higher performance.
- Fuels that work in PEMFCs are also applicable to AFCs, plus some new candidates. Major attention should be given to ethanol as a high energy density, widely available fuel. Breaking C-C bonds is a major challenge, but it is likely to be easier in alkaline media than in acidic media because of the wider range of stable catalytic materials. Work at Acta has already indicated the possibility of complete ethanol oxidation with high yield on catalysts that can only be used in alkaline media. Also, fuels such as $NaBH_4$, which are unstable in acidic media, are attractive candidates in alkaline media.
- Electrolyte Choice (CO_3^{2-}, OH^-, Membrane chemistry). The degree to which anion exchange occurs (conversion of OH- transporting membranes into carbonate-transporting membranes) will be a major factor in determining catalytic activity. The effects of pH, carbonate concentration, and water activity should be evaluated on promising catalytic materials to ensure stability and activity under the range of conditions likely to be encountered in AFCs.

Utilizing Anion Exchange Membranes in Fuel Cells

State of the Art: Alkaline fuel cells based on immobilized electrolytes or circulating electrolytes and KOH have been studied in depth for space and terrestrial applications. These approaches are still being pursued for niche applications, but the focus of this workshop is alkaline membranes and a critical barrier to the use of alkaline membrane fuel cells has been performance of membrane electrode assemblies. The two tables below (have been taken from the overview presentation of the principal investigator and) report performances of AEM fuel cells using either hydrogen (Table 2) or alternative fuels (Table 3).

Table 2. H_2/O_2 Alkaline Anion Exchange Membrane Fuel Cell Data

Membrane	**IEC (meq g^{-1})**	**Ionomer in Electrode**	**Anode Catalyst**	**Cathode Catalyst**	**T (^{o}C)**	**Peak Power Density (mWcm^{-2})**	**Current @ 0.5V (mAcm^{-2})**	**Ref**
AAEM*	1.14	crosslinked aminated poly(benzyl chloride)	4 mg cm^{-2} Pt	4 mg cm^{-2} Pt	50	1.6	4	6
AAEM*	1.14	crosslinked aminated poly(benzyl chloride)	0.5 mg cm^{-2} Pt/C	0.5 mg cm^{-2} Pt/C	50	55	110	26
AAEM*	1.14	crosslinked aminated poly(benzyl chloride)	0.5 mg cm^{-2} Pt/C	0.5 mg cm^{-2} Ag/C	50	49	80	26
AAEM*	1.14	crosslinked aminated poly(benzyl chloride)	0.5 mg cm^{-2} Pt/C	0.5 mg cm^{-2} Au/C	50	24	40	26
ETFE-based AAEM	1.42	crosslinked aminated poly(benzyl chloride)	0.5 mg cm^{-2} Pt/C	0.5 mg cm^{-2} Pt/C	50	90	175	27
ETFE-based AAEM	1.42	crosslinked aminated poly(benzyl chloride)	0.5 mg cm^{-2} Pt/C	0.5 mg cm^{-2} Pt/C	60	110	230	27
Epichlorohydrin-based AAEM	0.5-0.6	none	0.13 mg cm^{-2} Pt/C	0.13 mg cm^{-2} Pt/C	25	20	35	28
Epichlorohydrin-based AAEM	0.5-0.6	Polyacrylic acid and 1 M KOH	0.13 mg cm^{-2} Pt/C	0.13 mg cm^{-2} Pt/C	25	43	80	28

*benzyl chloride radiation-grafted membrane, converted to tetramethylammonium cation

Table 3. Alkaline Anion Exchange Membrane Fuel Cell Data using Liquid Fuels

Membrane	**IEC (meq g^{-1})**	**Anode Catalyst**	**Cathode Catalyst**	**Fuel**	**T (^{o}C)**	**Peak Power Density ($mWcm^{-2}$)**	**Current @ 0.5V (mA cm^{-2})**	**Ref**
ETFE-based AAEM[a]	1.42	4 mg cm^{-2} Pt-Ru	4 mg cm^{-2} Pt	2 M CH_3OH	50	1.5	-	27
ETFE-based AAEM[a]	1.42	4 mg cm^{-2} Pt-Ru	4 mg cm^{-2} Pt	2 M CH_3OH	80	8.5	5	27
Poly(4-vinyl pyridinium)	-	-	-	1 M CH_3OH	45	1.5	< 1	29
Morgane ADP	-	2 mg cm^{-2} Pt/C	2 mg cm^{-2} Pt/C	2 M CH_3OH 4 M NaOH	20	18	-	30
Morgane ADP	-	2 mg cm^{-2} Pt/C	2 mg cm^{-2} Pt/C	2 M HOC_2H_4OH 4 M NaOH	20	19	-	30
Morgane ADP	-	2 mg cm^{-2} Pt/C	2 mg cm^{-2} Pt/C	2 M CH_3OH	20	< 0.5	-	30
Morgane ADP	-	2 mg cm^{-2} Pt/C	2 mg cm^{-2} Pt/C	2 M CH_3OH 1M NaOH	60	11.7	10	31
Morgane ADP	-	1.5 mg cm^{-2} Pt/C	2 mg cm^{-2} Pt/C	2 M CH_3OH 1 M NaOH	60	7.0	5	32
Morgane ADP	-	1.2 mg cm^{-2} Pt/Ti mesh	2 mg cm^{-2} Pt/C	2 M CH_3OH 1 M NaOH	60	7.8	8	32
Morgane ADP	-	1.7 mg cm^{-2} Pt[c]	0.8 mg cm^{-2} Pt/C	2 M CH_3OH 1 M NaOH	60	17.8	10	33
Tokuyama AHA[b]	1.2	4 mg cm^{-2} Pt-Ru	1 mg cm^{-2} Pt/C	1 M CH_3OH 1 M KOH	50	6.0	7	34
Tokuyama AHA[b]	1.2	4 mg cm^{-2} Pt-Ru	1 mg cm^{-2} Pt/C	1 M HOC_2H_4OH 1 M KOH	50	9.5	12	34
Tokuyama AHA[b]	1.2	4 mg cm^{-2} Pt-Ru/C	1 mg cm^{-2} Ag/C	3 M HOC_2H_4OH 1 M KOH	50	8.1	4	34
Tosflex® SF-17	0.91	1 mg cm^{-2} Pt	1 mg cm^{-2} Pt	2 M $N_2H_4 \cdot H_2O$	60	-	15	35

[a] crosslinked aminated poly(benzyl chloride) in electrodes
[b] Poly(4-vinylpyridinium) in electrodes
[c] 1.2 mg cm^{-2} Pt on Ti mesh + 0.5 mg cm^{-2} deposited Pt on membrane

Current AEM fuel cell MEA design concepts have focused on two types of approaches: including a free electrolyte (KOH, K_2CO_3) in a liquid fuel; and incorporating an anion exchange polymer into the catalyst layer (applicable for gas or liquid fuel).[6,34] To this point the membranes used in such devices have used membrane materials developed for other applications and utilizing tetraalkylammonium cations and often polystyrene/divinylbenzene polymers.

The reported fuel cell performance of non-electrolyte containing fuels has been poor (see Tables), but significant gains have been realized by the incorporation of ionomer into the catalyst layer. Significantly, higher performances have been reported using free electrolyte/fuel solutions resulting in power densities and efficiencies that are attractive for devices.

A variety of fuels have been demonstrated: including ethanol, glycol, ammonia, hydrazine, and borohydride.[34,35] Ethanol oxidation has been reported using non-precious catalysts and relatively good performance. Operating temperatures up to 60 °C have reported durability over the period of several days. These demonstrations have not shown catastrophic effects due to carbonate formation.

Limitations: Chemical stability issues of AEMs are a key factor and have limited demonstration in fuel cells to below 60 °C. Full lifetime data (durability) is still lacking. A true understanding of device lifetime and system design is not available at this time.

The ability to operate AEM fuel cells without added electrolyte would be desired. To this point approaches to make highly performing electrodes have not been able to match the performance of free electrolyte containing systems. Improved electrode fabrication could allow for significant improvements in performance. Specific issues such as conductivity and catalyst efficiency/utilization need to be elucidated.

Systems that operate on hydrocarbon fuels will produce CO_2, and therefore carbonate will be produced. The effects of carbonate production are not understood, but may be important.

The use of free electrolyte has been shown to be advantageous for performance, however free electrolytes have limitations. They increase corrosion concerns, represent a potential handling and distribution problem and limit materials choices and introduce issues such as electrolyte balance while complicating water management.

Water management is a critical issue. AEMs have shown a higher dependence on relative humidity than acid based systems. The direction of electro-osmotic drag in these systems has an important effect on water management that could be positive (water balance, fuel crossover) or negative (decreased conductivity, chemical degradation). These factors are system/operation specific, but are not fully understood. The choice of gas diffusion layers in such systems will certainly be important.

Possible Approaches: Approaches to developing next generation AEM MEAs will likely focus on preparing electrode architectures that have suitable 3 phase boundaries that allow ionic and electronic conductivity plus the mass transfer characteristics necessary to produce a highly performing MEA without the need for free electrolyte in the fuel stream. These approaches will likely mimic the common PEM architectures that include Nafion based dispersions in the catalyst inks and have demonstrated high performance and catalyst utilization. Other electrode designs will have to be considered as well, as many of the advanced (non-platinum) catalysts effective in alkaline media have significantly different structure than the typical carbon supported or unsupported catalyst used in traditional PEM systems.

Water management in these systems seems to be even more critical in these systems for conductivity and stability. Backing layers and operating conditions will need to be explored in order to optimize performance and lifetime.

While extending lifetime and operating without free (added) electrolyte are goals for these systems, the potential cost/benefit analysis of short lived systems (disposable fuel cells or similar) or systems requiring electrolyte in the fuel (due to buffering capability, increased catalyst utilization, conductivity and lifetime considerations) needs to be investigated. In general, eliminating or managing KOH needs to be accomplished.

R&D Needs: In the area of utilizing anion exchange membranes in fuel cells the following are recommendations for research needs:

Higher Priority

- Developing advanced electrode architectures that allow ionic conductivity, electronic conductivity and good mass transport without the need for free electrolyte
    - Inks and electrode structures that mimic those of traditional PEMs
    - Novel architectures
- Systems Concerns
    - Determining operating conditions, lifetimes and performance of anion exchange membrane fuel cells
    - Evaluating effect of CO_2 in carbonate formation
    - Water balance and electrolyte management issues

Lower Priority

- Standardized durability and performance tests for materials evaluation
- Gas diffusion layer optimization

System Considerations/Needs

State of the Art: The systems aspects of fuel cell-based power sources of different scales for different applications are very wide ranging. Here we limit ourselves to discussion of the systems aspects of alkaline membrane fuel cell technology for compact power sources that produce 20-50 W, can operate for 72 hrs (possibly as long as 200 hrs), and have a specific energy of 700-1000 Whr/kg. Also, such systems should be able to survive / be operable over the temperature range of -40 to 55°C while being able to operate at 80°C internally. These alkaline membrane fuel cell systems should exceed the performance with state-of-the-art acidic DMFC technology. These criteria were set based on military needs and perceived advantages of alkaline fuel cell systems.

Presently two types of alkaline fuel cells have received more study; those that have an anion-exchange membrane as the electrolyte, and those that have a (flowing) liquid electrolyte of hydroxide or carbonate. In addition, some less developed concepts such as membraneless fuel cell designs and mixed feed fuel cells are being explored.

Limitations: Working in an alkaline environment may provide advantages with respect to reduced fuel crossover, efficiency, catalyst cost (non-noble vs. noble), lifetime (shelf & active), performance over a wide temperature range. In other words, alkaline fuel cell systems have the potential to overcome the limitations and issues related to the presently more mature acidic fuel cell technology.

For an alkaline fuel cell a wide range of fuels can be considered: Alcohols and derivatives (MeOH, EtOH, glycerol, iso-propanol), hydrides ($NaBH_4$, KBH_4, NH_3BH_3), and a few others (ammonia, hydrazine). In addition to the fuels themselves, also the properties (chemistries, safety) of the side products need to be considered. For example, hydrazine and ammonia may be less attractive of a choice because of their toxicity.

Eight main systems issues were identified. These will be discussed individually below mainly with the two dominant existing concepts of membrane-based systems and flowing electrolyte-based systems in mind. The main system considerations and a rough assessment of their relative importance for these two systems as well as for possible other systems (e.g. membraneless) is listed in Table 3 below.

Table 3. Comparison of membrane based systems, flowing electrolyte based systems and other approaches in terms of system issues.

		Anion Exchange Membrane	**Flowing Electrolyte**	**Others, e.g. membraneless**
I	MEA, membrane, stack, seals	Yes	Yes	Less so
II	Materials compatibility (corrosion etc)	Yes	More so	Yes
III	Dealing with CO_2 generated	Less so	Yes	Yes
IV	Water management	Yes	Easier	less so
V	Thermal management	Yes	Less so	Less so
VI	Shunt currents	Not really	Yes	Yes
VII	System / BOP considerations	Yes	More?	More?
VIII	Consume / replenish / refresh electrolyte	N.A.	Yes	Yes

Possibilities/ R&D Needs: In the area of systems, the possibilities and needs have been combined and are as follows:

-1- Membrane, MEA, Stack

The desired alkaline fuel system will obviously need components (e.g. membrane, MEA, Stack) that provide the performance characteristics and have the lifetime and stability to be a viable power sources in anticipated applications. The aspects of the membrane and MEA are discussed elsewhere in this report. Like in other fuel cell technologies the stack and the balance-of-plant components need to be integrated into a working fuel cell system. While the BOP for alkaline fuel cells will have different configurations/ requirements (see below), the basic integration of components challenge is no different than for an acidic system.

R&D recommendations: Alkaline fuel cells will require new/different materials for certain components, in particular, Nafion needs to be replaced with a different electrolyte. For anion exchange membrane-based systems, it is advised to first characterize any currently available materials to obtain a baseline performance. In particular, commercially available resins and membranes should be evaluated. In parallel the development of novel polymers for application as membranes in alkaline fuel cells should be explored. The latter is discussed in detail elsewhere in this report.

-2- Materials / components compatibility (Corrosion resistance etc.)

The alkaline environment is rather harsh in nature, and all components of the system that are in contact with the alkaline environment/electrolyte need to be compatible with strong base. Particularly, attention should be paid to seals in the stack and elsewhere, bipolar plate materials, hardware, tubing, BOP materials & components.

-3- Dealing with CO_2

Dealing with carbon dioxide from air at the cathode side is not seen as a significant issue. In contrast, the situation is less clear on the fuel side. Carbon dioxide could form insoluble carbonates that would lead to detrimental effects such as membrane clogging and catalytic site blockage.

R&D recommendations: The interaction of the various carbonate species with the membrane, catalyst surface, as well as the MEA in general needs to be explored for the anion exchange membrane-based systems.

The carbonate problem is more serious in the flowing electrolyte systems due to the inevitable interaction between strong base and acidic carbon dioxide.

R&D recommendations: A detailed investigation of all equilibria and kinetics between all carbonate species in the electrolyte should be made as function of time, performance, and temperature.

-4- Water Management

Water management is seen as a major system issue for alkaline fuel cells with respect to (i) appropriate hydration of the electrodes, in particularly the cathode; and (ii) removal of the excess water that is formed during the cell reaction and would otherwise accumulate in the system. The cathode can be provided with sufficient water in two ways: First, the migration of water through the electrolyte from the anode to the cathode, and second, the transport of water to the cathode from anywhere in the system to the cathode. The first one would be preferred because of simplicity of design.

R&D recommendations: We recommend that the water flux due to diffusion and electro-osmotic migration through existing as well as novel membranes will be studied in detail. In addition, external means of humidification of the cathode should be explored. We also note that from the point of reducing parasitic losses, one would like to minimize the air flow past the cathode, but this would complicate the removal of excess water. That water would now need to be removed by other means, requiring the development of a detailed water balance strategy. Also, the impact of the hydrophilic/hydrophobic character of membrane materials needs to be investigated in light of differences in water content in the membrane as a result of operation in alkaline media (wettability depends on pH).

-5- Thermal Management

For the overall alkaline fuel cell system an efficient heat management strategy needs to be defined. Excess heat needs to be removed to avoid overheating of the system, even if the system needs to operate in an environment with a high ambient temperature (e.g. 55°C in desert environments).

R&D recommendations: Keeping in mind that a compact power source operating at 0.6V per single cell with a current density on the order of 150 mA/cm2 is desired, appropriate heat removal designs need to be explored, as well as the use of efficient pumps and blowers. All sources of heat should be characterized, including the waste heat from the stack and all parasitic losses from balance-of-plant components (pumps, blowers, electronics). Given the compact size of the envisioned power source, there may be room for novel concepts of heat removal.

-6- System

Overall system configurations of both the stack and the BOP differ significantly for different fuel cell types. The two main alkaline fuel cell systems (‘membrane’ and ‘flowing electrolyte’) already differ significantly.

R&D Recommendations: Fuel cell system design often starts with optimizing steady state operation under optimal conditions, yet start-up and shut-off as well as operation under non-optimal ambient conditions needs to be taken into account as well. Related to that, system controllers that use input from internal sensors (e.g. fuel, electrolyte state) and external sensors (e.g. temp, humidity, orientation wrt. gravity, pressure especially related to altitude) need more attention.

-7- Shunt Currents

The issues with shunt currents have already been addressed in various other fuel cells an battery systems with flowing electrolytes and would be no different for an alkaline based system with the exception that the conductivity may differ. So this issue is not specific to alkaline fuel cell technology and thus no specific efforts in this area are recommended. The Stack designer will take care of this.

-8- Consume / replenish / refresh electrolyte (flowing electrolyte)

In the flowing electrolyte-based alkaline fuel cells special attention must be given to the condition of the electrolyte over time. Due to the carbon dioxide related issues described above, hydroxide ions will be depleted. The formed carbonates, initially soluble in the electrolyte, may precipitate as solids either as a consequence of accumulation from the cell reaction or because of a decrease in cell temperature in the system (e.g. during shut down). Similarly, side-products of fuel oxidation and pollutants from air may end up in the electrolyte stream over time.

R&D recommendations: The recirculation of electrolyte should be further explored in light of its changing composition over time. To reduce parasitic losses, passive means of driving the recirculation should be evaluated, which may be particularly appropriate at the envisioned scale. In addition, other ways to refresh or regenerate the electrolyte should be explored; electrochemical cleaning was mentioned as a possibility. Also, the use of carbon-free fuels could be explored, since that would eliminate the major source of the CO_2, the source of many of the electrolyte degradation issues.

References

The list of references supports the text of the report, but by no means, is intended to be exhaustive. Significantly more references are reported in the individual presentations from the workshop and in many cases references were limited to "best" examples. Of note, reference 5 is a good review of alkaline membrane fuel cell technology, albeit a couple of years old.

---

[1] S. Thomas and M. Zalbowitz, *Fuel Cells: Green Power*, Los Alamos National Laboratory, Los Alamos, NM, **1999**.

[2] G.J.K. Acres, *J. Power Sources*, 2001, **100**, 60.

[3] B. Pivovar, *Polymer*, 2006, **47**, 4194.

[4] D.J. Berger, *Science*, 1999, **286**, 49.

[5] J.R. Varcoe and C.T. Slade, *Fuel Cells*, 2005, **5**, 187.

[6] J.R. Varcoe, R.C.T. Slade and E.L.H. Yee, *Chem. Comm.*, 2006, **13**, 1428.

[7] K. Kneifel and K. Hattenbach, *Desalination*, 1980, **34**, 77.

[8] B. Bauer, F.J. Gerner and H. Strathmann, *Desalination*, 1988, **68**, 279.

[9] B. Bauer, H. Strathmann and F. Effenberger, *Desalination*, 1990, **79**, 125.

[10] V. Neagu, I. Bunia, and I. Plesca, *Polymer Degradation and Stability*, 2000, **70**, 463.

[11] A.A. Zagorodni, D.L. Kotova and B.F. Selemenev, *Reactive and Functional Polymers*, 2002, **53**, 157.

[12] T. Sata, M. Tsujimoto, T. Yamaguchi and K. Matsusaki, *J. Membr. Sci.*, 1996, **112**, 161.

[13] R. Schwesinger, R. Link, P. Wenzl, S. Kossek and M. Keller, *Chem. Eur. J.*, 2006, **12**, 429.

[14] Y.S. Kim, J. McGrath and B. Pivovar, *Abstracts of the 206th Electrochemical Society Meeting*, 2004, **2004-02**, 1471.

[15] A. Roy, M.A. Hickner, X. Yu, Y. Li, T.E. Glass and J.E. McGrath, *J. Polym. Sci. Part B: Polym. Physics*, 2006, **44**, 2226.

[16] G. Alberti and M. Casciola, *Annu. Rev. Mater. Res.*, 2003, **33**, 129.

[17] G. F. McLean, T. Niet, S. Prince-Richard and N. Djilali, *International Journal of Hydrogen Energy*, 2002, **27**, 507-526.

[18] A. Verma and S. Basu, *Journal of Power Sources*, 2005, **145**, 282-285.

[19] K. Kinoshita, *Electrochemical Oxygen Technology*, Wiley, New York, 1992.

[20] K. Okajima, K. Nabekura, T. Kondoh and M. Sudoh, *Journal of the Electrochemical Society*, 2005, **152**, D117-120.

[21] K. Sawai and N. Suzuki, *Chemistry Letters*, 2004, **33**, 1540-1541.

[22] M. L. Calegaro, F. H. B. Lima and E. A. Ticianelli, *Journal of Power Sources*, 2006, **158**, 735-739.

[23] J. Zhang, F. H. B. Lima, M. H. Shao, K. Sasaki, J. X. Wang, J. Hanson and R. R. Adzic, *J. Phys. Chem. B*, 2005, **109**, 22701-22704.

[24] V. Stamenkovic, B. S. Mun, K. J. J. Mayrhofer, P. N. Ross, N. M. Markovic, J. Rossmeisl, J. Greeley and J. K. Norskov, *Angewandte Chemie - International Edition*, 2006, **45**, 2897-2901.

[25] M. S. Wilson and S. Gottesfeld, *Journal of Applied Electrochemistry*, 1992, **22**, 1-7.

---

[26] J.R. Varcoe, R.C.T. Slade, G.L. Wright and Y. Chen, *J. Phys. Chem. B*, 2006, **110**, 21041.

[27] J.R. Varcoe and R.C.T. Slade, *Electrochem. Comm.*, 2006, **8**, 839.

[28] E. Agel, J. Bouet and J.F. Fauvarque, *J. Power Sources*, 2001, **101**, 267.

[29] A. Huang, C. Xia, C. Xiao and L. Zhuang, *J. Appl. Polym. Sci.*, 2006, **100**, 2248.

[30] C. Coutanceau, L. Demarconnay, C. Lamy and J.-M. Leger, *J. Power Sources*, 2006, **156**, 14.

[31] E.H. Yu and K. Scott, *J. Power Sources*, 2004, **137**, 248.

[32] E.H. Yu and K. Scott, *Electrochem. Comm.*, 2004, **6**, 361.

[33] E.H. Yu and K. Scott, *J. Appl. Electrochem.*, 2005, **35**, 91.

[34] K. Matsuoka, Y. Iriyama, T. Abe, M. Matsuoka and Z. Ogumi, *J. Power Sources*, 2005, **150**, 27.

[35] K. Yamada, K. Yasuda, H. Tanaka, Y. Miyazaki and T. Kobayashi, *J. Power Sources*, 2003, **122**, 132.