

Progress in preparation of non-noble electrocatalysts for PEM fuel cell reactions

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Received 23 February 2005; accepted 3 May 2005

Available online 25 July 2005

Abstract

This paper reviews the literature on the preparation aspect of non-noble electrocatalysts for PEM fuel cell reactions, especially focusing on cathode electrocatalyst preparation methods. Various effective synthesis methods for two kinds of promising catalysts such as transition metal chalcogenides, and heat-treated nitrogen containing complexes (macrocyclic complexes) are discussed. Though some remarkable progress has been made in catalyst preparation techniques, neither of these catalysts has reached the level of a Pt based catalyst in terms of catalytic activity, durability and chemical/electrochemical stability. In order to make non-noble electrocatalysts commercially feasible, cost-effective and innovative, catalyst synthesis methods are needed for new catalyst discovery and catalyst performance optimization. Crown Copyright © 2005 Published by Elsevier B.V. All rights reserved.

Keywords: Chemical synthesis; Non-noble electrocatalysts; Oxygen reduction; PEM fuel cells

1. Introduction

Polymer electrolyte membrane (PEM) fuel cells, as the energy converting devices, have drawn a great deal of attention in both aspects of fundamental and application in recent years [1,2]. For application in the areas of transportation, stationary, portable and micro power fuel cells have unique and favourable advantages over chemical batteries in terms of high efficiency, high energy density, zero or low emission. However, in the path towards fuel cell commercialization, one of the big challenges is to reduce the material cost. One of the major contributors to the high cost is the platinum based catalyst. Some solutions for catalyst cost reduction have been put forward, and the corresponding research and development have been carried on for many years, however, there have been no breakthroughs up to this time [3–5]. In order to reduce the cost of the fuel cell catalysts, two approaches are currently very active: exploration of non-noble catalysts, and

reduction of the Pt loading [6,7]. With respect to non-noble catalysts, there have been no significant breakthroughs in the areas of materials and technology. In the aspect of Pt loading reduction, although some promising approaches and results have been reported for Pt loading reduction, the lifetime of a low Pt loading fuel cell is still problematic. Therefore, there exists a large area of research for making improvements and progress in this field.

Using a Pt based catalyst, fuel cell performance is usually limited by the slow kinetics of cathode oxygen reduction (mass transfer of O₂ is not considered here). Compared to the anode hydrogen oxidation reaction, which has a small overpotential of <25 mV, the cathode oxygen reduction exhibits a larger overpotential (this can be over 300 mV for a moderate range of current density, <1.0 A cm⁻²) [8]. Therefore, this review will focus on electrocatalysts for cathode oxygen reduction.

Platinum based particle catalysts including black Pt powders and carbon supported Pt particles are the most active, efficient, applicable and successful catalysts for fuel cell reactions at the current technology stage. However, there are

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several drawbacks to using Pt catalysts in a fuel cell, beside the high cost issue.

- (1) Pt catalyzed cathode oxygen reduction is not a complete four-electron reaction. It is well known that the oxygen reduction reaction is a complex process that includes many electrochemical (chemical) steps with different intermediates [9]. Oxygen electroreduction mainly proceeds by two pathways: a direct four-electron reduction of oxygen that produces H_2O , and a two-electron reduction of oxygen yielding H_2O_2 , which may be further reduced to H_2O . A two-electron reduction of oxygen not only reduces the efficiency of the system, the strong oxidation that is associated with the produced hydrogen peroxide can degrade the catalytic activity of catalysts [10–12]. The hydrogen peroxide radicals produced by the two-electron reduction of O_2 can also attack the catalyst carbon layer and the proton exchange membrane (and/or ionomer in the catalyst layer), resulting in significant fuel cell degradation, and even failure. Therefore it is necessary to find an effective catalyst that can promote the direct four-electron reduction of oxygen to give H_2O , in order to improve the efficiency of PEM fuel cell.
- (2) Pt catalysts are very sensitive to contaminants in the feed system. Fuel cell contamination caused by the impurities in the feed stream such as CO , H_2S , NH_3 , organic sulfur–carbon and carbon–hydrogen compounds in H_2 stream, NO_x , and SO_x in the air stream, is an important issue in fuel cell development and operation [13,14]. These impurities or contaminants can easily poison the Pt catalyst, resulting in performance degradation.
- (3) A cathode platinum catalyst has no inertness to methanol oxidation in a direct methanol fuel cell (DMFC). In a DMFC, methanol crosses through the membrane from the anode to the cathode, and then reacts with the cathode Pt catalyst, leading to a cathode potential drop, which lowers the operating cell voltage [15,16]. This activity of cathode Pt toward methanol oxidation is not desirable. Some metal macrocyclic complexes such as Fe and Co porphyrins or phthalocyanines have been tested as DMFC cathode catalysts. They showed remarkable selectivity to O_2 reduction and inertness to methanol oxidation.

There has been significant activity in recent years in oxygen electrochemistry to develop new and low-cost, non-noble, metal-based electrocatalysts, which would be capable of selectively catalyzing the four-electron reduction of oxygen to produce water with low overpotential and low H_2O_2 -production, a greater tolerance of contaminants, and the ability to remain inert during cathode methanol oxidation in DMFCs.

Various materials have been proposed as non-noble cathode catalysts. Transition metal oxides, especially those with a perovskite or pyrochlore structure that allows easy exchange of oxygen, showed remarkable activity for oxygen reduction in an alkaline solution. Unfortunately, most transition metal

oxides have been found to be unstable in the acidic environment of PEM fuel cell operation. Reeve et al. observed that in acidic solutions, the activity declined substantially, and the stability of the oxide phase was also very poor. The slow dissolution of metal components of the oxide and their re-deposition at the anode caused severe cumulative poisoning problems [17].

Since Alonso-Vante et al. initially proposed that semi-conducting chevre-phase Ru–Mo chalcogenides (sulfides, selenides) had significant oxygen reduction activity in acid conditions [18], some transition metal chalcogenides have been investigated as promising non-noble catalysts. These materials are also of interest in aspects of fundamental research. It has been found that the delocalization of electrons in a metal cluster can lead to a high electron conductivity and attenuate the relaxation of the electronic states. The availability of a reservoir of charges for the multi-electron charge transfer is also very important for enhancing catalytic activity. The unique feature of chalcogenides is the high stability in an acidic environment, especially if in combination with other transition metals [19–21].

It has been known that transition metal (e.g., Fe, Co) macrocyclic compounds (e.g., porphyrins, phthalocyanines, tetraazannulenes) could be used as electrocatalysts for oxygen reduction since Jasinski's discovery of the catalytic properties of Co phthalocyanine [22]. However, they show low electrochemical (chemical) stability in acidic conditions. The decomposition either via hydrolysis in the electrolyte, or an attack of the macrocycle rings by peroxide intermediates was found to be the main cause of the poor stability. Attempts to improve both catalytic activity and stability has led to the discovery that heat-treatment of transition metal macrocycles ($>800^\circ\text{C}$) can significantly improve stability and, in some circumstances, enhance overall catalytic activity [23–34].

Some work has been done on copper and iron surface complexes for oxygen electroreduction catalysts [35–40] and these surface complexes have been observed to catalyze the reaction through a dominating four-electron reduction pathway from O_2 to water. Unfortunately, the onset electrode potentials for oxygen reduction catalyzed by these surface complexes were much more negative than that catalyzed by a Pt based catalyst, therefore the feasibility of employing these complexes as the fuel cell cathode catalysts would be limited. However, it will be very useful to continue this approach to gain a fundamental understanding of the reaction mechanism.

At present, exploration for new non-noble catalysts is very active, and results show some remarkable catalytic activity toward O_2 reduction. Although the catalytic activity has not matched that of Pt catalysts, it will continue to approach that level. Transition metal chalcogenides and pyrolyzed macrocyclic compounds are two of the most widely studied non-noble metal catalysts for PEM fuel cell oxygen reduction. At this stage, the first priority for fuel cell catalyst development is to explore new catalysts and enhance catalytic activity through some innovative ways of preparation and synthesis. The purpose of this review is to give an overview of the

chemical synthesis and the preparation of these two kinds of non-noble catalysts. Various synthesis and preparation routes are reviewed, with emphasis on the problems and prospects associated with the different methods.

2. Transition metal chalcogenides

Two major transition metal chalcogenides have been explored as electrocatalysts for fuel cell oxygen reduction: Chevrel phase-type compounds (e.g., $\text{Mo}_4\text{Ru}_2\text{Se}_8$) and amorphous phase compounds (e.g., $\text{Ru}_x\text{Mo}_y\text{Se}_z$, Ru_xS_y).

2.1. Chevrel phase-type compounds [18,19,41,42]

These compounds have a cluster structure with a repeating crystal lattice containing a metal ion cluster in the centre, surrounded by several non-metal ions. For example, in a binary compound of M_6^1X_8 (M^1 = high valent transition metal, e.g., Mo; X = chalcogen, e.g., S, Se, Te), each lattice contains a central octahedral metal cluster with six metal ions surrounded nearly cubically by eight chalcogen ions. There are also ternary compounds such as $\text{Mo}_6\text{M}_x^2\text{X}_8$ (M^2 = intercalated metal guest ion), and pseudobinary compounds such as $\text{Mo}_6\text{M}_x^3\text{X}_8$ (M^3 = foreign metal ions which replace the Mo in octahedral M^1 cluster). Cluster compounds of this type were tested as electrocatalysts for oxygen reduction. All of them appeared to have some level of activity. The $\text{Mo}_6\text{M}_x^2\text{X}_8$ compound was found to be electrochemically unstable due to deintercalation at positive electrode potentials. Extensive studies were focused on the mixed transition metal cluster compounds ($\text{Mo}_6\text{M}_x^3\text{X}_8$, called pseudobinaries). When M^3 = Ruthenium (Ru), this compound displayed the best activity among other metals tested. Alonso-Vante et al. observed that $\text{Mo}_{6-x}\text{Ru}_x\text{X}_8$ could catalyze the electroreduction through a four-electron pathway from O_2 directly to H_2O . This remarkable activity was attributed to the presence of octahedral mixed metal clusters. These clusters might act as reservoirs for electron transfer from the electrode to coordinated O_2 on the clusters, see Fig. 1 [43].

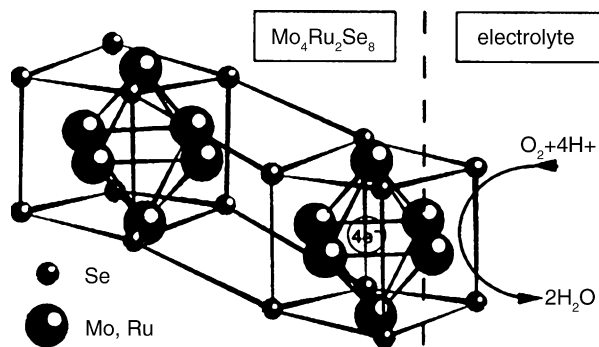


Fig. 1. Interaction of molecular oxygen in acid medium at the Chevrel phase clusters–electrolyte interface [43].

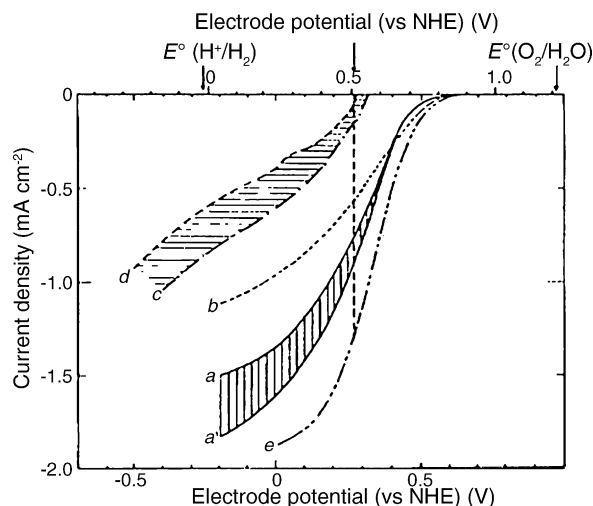


Fig. 2. Catalytic effect of oxygen reduction on several cluster compounds and Pt in 0.5 M H_2SO_4 at $\omega = 400$ rpm, $\nu = 5$ mV s^{-1} . (a) $\text{Mo}_{4.2}\text{Ru}_{1.8}\text{Se}_8$; (b) $\text{Mo}_{3.7}\text{Ru}_{2.3}\text{Se}_8$; (c and d) $\text{Ni}_{0.85}\text{Mo}_6\text{Te}_8$; (e) Pt. At the top the thermodynamic potentials of H_2 and O_2 are shown for this medium (pH 0.3). The arrow placed at 0.51 V/NHE (overpotential = 0.7 V) indicates the working conditions in a fuel cell, (c and d) indicate electrodes with less and more Ni at the surface, respectively. NHE is the normal hydrogen electrode; SCE is the saturated calomel electrode ([18], with Nature's copyright permission).

It was also observed that the clusters could change volume during the reduction process. When the cluster lost four electrons, metal–metal bonds became weaker which increased cluster volume by approximately 15%. At this stage, $\text{Mo}_4\text{Ru}_2\text{Se}_8$ was found to be one of the best non-platinum oxygen reduction catalysts for PEM fuel cell reactions. Compared to the metal macrocyclic complexes such as iron and/or cobalt porphyrins and phthalocyanines, $\text{Mo}_{6-x}\text{Ru}_x\text{X}_8$ catalysts seemed to be more promising. For example, at a normal voltage range of the fuel cell operation, $\text{Mo}_4\text{Ru}_2\text{Se}_8$ was inferior to Pt catalyst by only 30–40%. Fig. 2 shows the catalytic properties of several $\text{Mo}_{6-x}\text{Ru}_x\text{X}_8$ catalysts for oxygen reduction, where $\text{Mo}_{4.2}\text{Ru}_{1.8}\text{Se}_8$ closely approaches the level of Pt catalyst [18]. It was expected that further optimizing the catalyst layer structure might lead to an improvement in catalyst performance.

$\text{Mo}_4\text{Ru}_2\text{Se}_8$ was synthesized via a high-temperature solid-state reaction by heating stoichiometric amounts of high-purity elements in sealed quartz ampoules for 24 h at 1470 K. The solid powder formed was melted at 1970 K for another 48 h in a high-pressure (0.7 GPa) argon filled furnace. After cooling, loose powder was agitated in an ampoule. In order to obtain a homogeneous product, the powder was again thermally treated at 1970 K for 120 h. The final product was analyzed, and a 4% impurity was found in the powder.

As discussed above, chevrel phase-type compounds seem to display some remarkable electrocatalytic activities toward oxygen reduction, and their activities could be affected by the content and nature of foreign metal ions in the cluster. However, now Alonso-Vante rarely cites his pioneering paper published in Nature, in which he initially proposed

that semi-conducting chevrel-phase Ru–Mo chalcogenides (sulfides, selenides) had significant oxygen reduction activity in acid conditions [18]. The main reason could be that the chevrel phases may not be the dominating active sites for oxygen electroreduction although the nominal compositions were the same as the chevrel phases. This will be further discussed in the following part of this section. Nevertheless, this pioneering work is important and it opened a new area of catalysis.

2.2. Amorphous transition metal chalcogenides

The process for catalyst synthesis by means of high-temperature solid-state reaction was complicated and costly. It required an environment of extremely high temperatures in a vacuum, where undesired by-products were formed. New synthesis routes that are operated under moderate conditions are definitely needed in order to simplify the process, reduce costs and allow the production of transition metal chalcogenides at lower temperatures in the form of nanoparticles whose size and shape can be controlled.

Again, it is Alonso-Vante et al. [21,42] who proposed and validated a new low temperature chemical precipitation method through mixing metal carbonyls and the corresponding chalcogen in an organic solvent such as xylene or 1,2-dichlorobenzene. Careful examination on the $\text{Mo}_x\text{Ru}_y\text{SO}_z/\text{Mo}_x\text{Ru}_y\text{SeO}_z$ and $\text{Ru}_x\text{S}_y/\text{Ru}_x\text{Se}_y$ systems [17,44–46] revealed that the formed compounds had a polycrystalline and amorphous structure rather than a chevrel structure. The reaction products consist of nano-scale Ru-metals and octahedral clusters of Ru, which contain carbon in the centre, surrounded by carbonyl groups. Ruthenium/carbide/carbonyl compounds are expected to be the active center. These complexes do not form a crystalline compound, but they are present as a film on the ruthenium colloids. A schematic drawing depicting such structural catalyst is shown in Fig. 3 [47].

This structure probably resulted from the mild synthesis temperature (e.g., 140 °C) [48]. Catalyst synthesized by this low temperature chemical precipitation method (e.g., $\text{Mo}_x\text{Ru}_y\text{SeO}_z$) showed an efficient electrocatalytic activity towards oxygen reduction in acid medium [42,45]. The precipitation process was performed in an argon atmosphere at 140 °C for ~20 h. Chemicals such as molybdenum hexacarbonyl, trisruthenium dodecacarbonyl and selenium were mixed in a dried-xylene solution, which was constantly stirred and refluxed. The obtained precipitator was filtered and washed with dried-diethylether and then dried in the air. The synthesis temperature depended on the boiling point of the solvent used, e.g., 140 °C for xylene and 180 °C for 1,2-dichlorobenzene [49–52]. The flow chart of this low temperature chemical precipitation method for the synthesis of Ru-based chalcogenides is given in Fig. 4. It was found that if the synthesis was operated in an aprotic solvent, the precipitator particle size were at a nanoscale. However, because this method involved some complex chemical reactions, a mixture

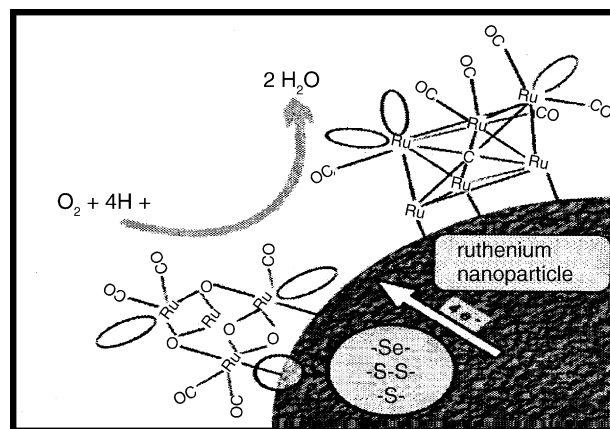


Fig. 3. Proposed qualitative structure of carbon modified Ru-catalyst. Possible interfacial Ru-clusters are shown grown on a Ru-nanparticle. The cubane-like Ru-complex has been selected as a model system to describe the interaction of chalcogene with Ru-clusters during oxygen reduction. Selenium or sulphur may act as a bridge to transfer electrons between the Ru-complexes and the colloids [47].

containing several polynuclear compounds with amorphous structures could be produced, depending on the synthesis temperature. It was very difficult to separate and characterize this mixture by traditional chemical methods, due to their small solubility, which was probably one of the drawbacks of this synthesis method. Another disadvantage of this method could be that the yield of the final product was always below 100% (normally ~40–60%) [53].

Several groups such as Hammnet [17,45], Sebastian [54–56], and Tributsch [57,58] carried out the same synthesis process using Ru-based electrocatalysts for oxygen reduction. Hammnet et al. [17] found that carbon-supported MRu_5S_5 ($M = \text{Rh}$ or Re) could give the best electrocatalytic activity. It was even better than that of $\text{Mo}_4\text{Ru}_2\text{Se}_8$ synthesized by a high-temperature solid-state reaction. The study by Schmidt et al. [59] showed that a carbon-supported $\text{Ru}_x\text{Mo}_y\text{SeO}_z$ had similar catalytic activity to a carbon-supported Ru catalyst, suggesting that only the pure ruthenium formed the catalytic site and that both Mo and Se probably did not participate in the electrocatalysis process. However, Bron et al. [47,60] demonstrated that the presence of selenium may have acted as a bridge to facilitate efficient electron transfer between the Ru-complexes and the colloids, while protecting the catalysts from the electrochemical oxidation through surface modification of the catalyst by carbonyl and carbide–carbonyl complexes or carbon compounds, which led to an enhanced stability.

Solorza-Feria et al. [61,62] proposed a new low temperature pyrolysis route at a synthesis temperature of 300 °C. The catalysts that were produced showed good stability and electrocatalytic activity for oxygen reduction in acidic medium. The synthesis was performed by pyrolyzing a mixture of $\text{Ru}_3(\text{CO})_{12}$ and elemental sulphur in a sealed glass ampoule at 300 °C for 24 h. The resulting powder was rinsed twice with a 1:1:1 mixture of hexane, chloroform and ethyl acetate

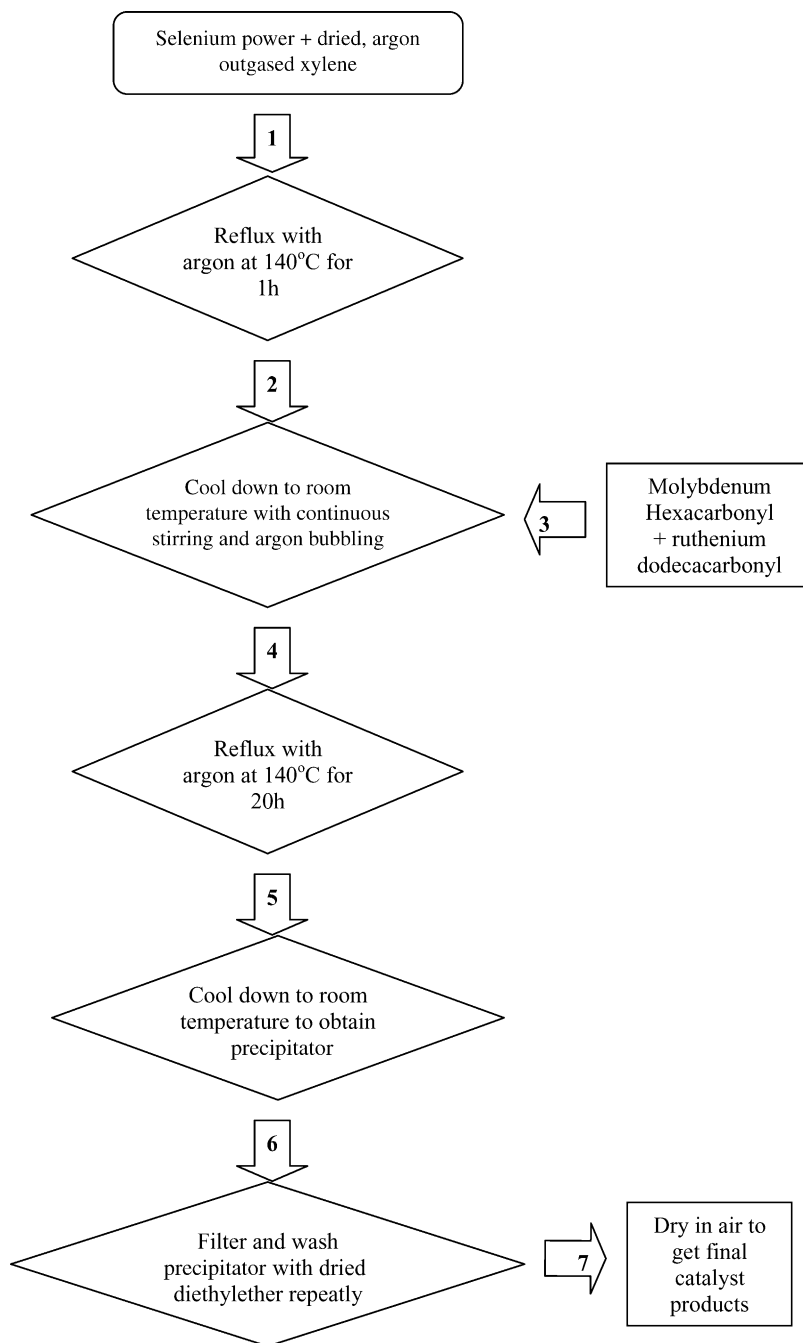


Fig. 4. Flow chart of Ru-based chalcogenides synthesized by low temperature chemical precipitation method.

to remove unreacted reactants. The powder was then dried overnight at 120 °C. The final amorphous product, $\text{Ru}_x\text{S}_y(\text{CO})_n$, was tested for O_2 electroreduction, and some considerable catalytic activity was found. It seemed that the heating temperature played an important role in the synthesis process in order to produce a better catalyst. Tributsch et al. [47] found a reduction in catalytic activity of heated, unsupported $\text{Mo}_x\text{Ru}_y\text{SeO}_z$ after release of carbon monoxide and carbon dioxide (between 250 and 350 and above 600 °C). Based on this, Tributsch et al. assumed that the high catalytic activity of their catalysts was due to an interaction of

ruthenium and carbon ligands. One possible reason for this is that the carbon species may stabilize the Ru metal interface by preventing Ru particles from rapidly transforming into RuO_2 in an exothermic reaction. The other effect of carbon species may be the alteration of the distribution of interfacial electronic states, which is caused by the formation of Ru-complexes. Trapp et al. [44] also found an improved activity of heated carbon-supported Ru-based catalysts at a temperature of 350 °C. More recent work by Campbell showed that heating the carbon-supported Ru_xSe catalyst at 600 °C completes the reaction between the ruthenium and selenium and

causes decarbonylation. Even when the heating temperature was as high as 600 °C, catalyst activity was not compromised if the carbon species was present.

More recently, Campbell disclosed an environment-friendly aqueous method for preparing active catalysts such as Ru_xSe . As suggested in the patent publication [63], it was not necessary to use expensive starting material of $\text{Ru}_3(\text{CO})_{12}$ and the toxic solvent xylene for the synthesis. He proposed a mixture of active carbon, ruthenium (III) chloride and selenium dioxide in a water/propanol solvent with constant stirring at 80 °C for 1 h. The resulting mixed solution was then allowed to cool at room temperature. An aqueous solution of NaOH containing NaBH_4 was then added to the solution to carry out the chemical reduction reactions. The excess NaBH_4 was removed by heating the mixture to 80 °C for 5 min. The formed powder was filtered and washed in water and dried overnight at 80 °C. The dried powder was then placed in a quartz lined tube furnace under nitrogen and heated to 600 °C for 2 h. In this way, a carbon-supported catalyst, which has a chemical formula of Ru_xSe , was produced and tested for oxygen reduction in an electrochemical environment. It claimed that the electrocatalytic activity of this carbon-supported Ru_xSe catalyst was very close to that of carbon-supported platinum catalysts. Fig. 5 illustrates a corrected Tafel plot for oxygen reduction carbon-supported catalysts in 0.5 M sulphuric acid at room temperature for the purpose of comparison [63].

Traditional impregnation is another method of catalyst preparation. One possible drawback of this method is that the temperature used to sinter the catalyst particles is relatively high, which could reduce the catalyst active area. In this impregnation process for Ru_xSe_y synthesis [64], a solution of ruthenium oxalate or carbonyl was mixed with a carbon support to form slurry, which was then dried to remove the solvent. The formed solid was then heated to decompose the salt, in order to produce the desired form of solid carbon-Ru

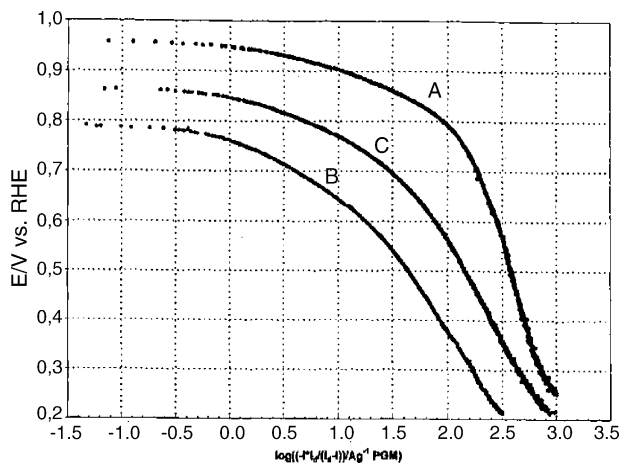


Fig. 5. Corrected Tafel plot comparing the activities of supported Ru_xSe with platinum and elemental ruthenium catalysts for oxygen reduction in acid medium at room temperature. (A) 40% Pt on XC72R carbon; (B) 40% Ru on XC72R carbon; (C) 40% Ru_xSe on XC72R carbon [63].

salt. For selenium incorporation, the solid was dispersed in a solution containing H_2SeO_3 . After the chemical reaction between the carbon-Ru salt and H_2SeO_3 , a Ru_xSe_y catalyst was produced.

The low temperature chemical precipitation method [45] described above has the advantage of allowing the reaction performed in a solution to form bimetallic catalysts at low temperature. The prepared catalysts normally have a higher active area. However, this method was limited to those reactants with similar precipitation chemistry or property, which are easily reduced chemically to metals. In order to minimize this limitation, a colloid method was developed, although the reproducibility was relatively low [47,65]. The first step for the catalyst synthesis was to make colloidal Ru nanoparticles through RuCl_3 reduction in a solution of tetrahydrofuran (THF) containing $\text{N}(\text{C}_8\text{H}_{17})_4\text{Bet}_3\text{H}$, followed by an addition of absolute ethanol liquid. After that, the mixture was centrifuged to obtain the solid powder. After the incorporation of selenium, $\text{Ru}_x\text{Se}_y\text{O}_z$ nanoparticles were prepared. The produced catalyst was tested for O_2 reduction and a fairly high electrocatalytic activity was observed. The high catalytic activity has been attributed to its large surface area, narrow particle size distribution, and abilities to prevent particle aggregation.

Several synthesis methods for O_2 electrocatalytic reduction were summarized and highlighted in Table 1 with some qualitative data for the purpose of comparison.

3. Macrocyclic complexes

A large variety of transition metal (e.g., Fe and Co) macrocyclic complexes such as N_4 -, N_2O_2 -, N_2S_2 -, O_4 - and S_4 -systems all showed a certain level of catalytic activity for oxygen reduction [66]. It is well known that N_4 -chelates of transition metal such as iron- and cobalt-porphyrins, phthalocyanines, and tetraazannulenes are the most popular active catalysts for oxygen reduction. This could be partially attributed to the inductive and mesomeric effects of the ligands on the central ion. Materials in this class of non-noble catalysts were also considered as the most promising materials to replace the expensive noble metal Pt catalysts in a PEM fuel cell [66]. Beck et al. [67] proposed that the mechanism of the electroreduction of oxygen catalyzed by N_4 -chelates of transition metal was mainly involved by a modified 'redox catalysis'. The first step in the oxygen reduction was the adsorption of oxygen on the catalyst metal center to form an oxygen-catalyst adduct, followed by electron transfer from the metal center to bound O_2 and the regeneration of the reduced N_4 -chelates as the following steps [67]

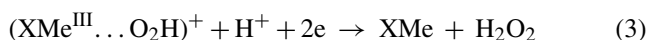
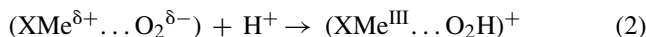
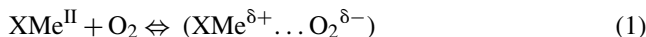


Table 1
Preparation methods for transition metal chalcogenide catalysts for oxygen electroreduction

Methods	Starting chemicals	Operating environment	Typical catalysts	Catalytic activity toward O ₂ reduction vs. Pt activity ^a	Refs.
High-temperature solid-state reaction	High purity transition metals and chalcogen	1000–1200 °C, 0.7 Gpa, sealed quartz ampoules with argon	Chevrel phases Mo _{6-x} Ru _x Se ₈ , where $x = 1.8$	~60%	[18,19]
Low-temperature chemical precipitation reaction	Metal carbonyls and chalcogen	140–180 °C, organic solvent with argon	Amorphous phases Mo _x Ru _y SeO _z	~23%	[44,47]
Low-temperature pyrolysis method	Metal carbonyls and chalcogen	300 °C, sealed glass ampoule	Amorphous phases Ru _x S _y (CO) _h	N/A	[61,62]
Aqueous medium method	Metal salts, chalcogen oxides and Sodium borohydrides	80 °C, aqueous solvent	Amorphous phases Ru _x Se	~27%	[63]
Traditional impregnation method	Metal carbonyls or oxalates and selenous acid	300 °C, aqueous solvent	Amorphous phases Ru _x Se _y	~10%	[64]
Colloid method	Metal chlorides and chalcogen	Room temperature, THF solvent with N(C ₈ H ₁₇) ₄ BEt ₃	Amorphous phases Ru _x Se _y O _z	~20%	[47,64,65]

^a The ratio of catalytic current density to that produced by Pt catalysts at 0.6 V(vs. SHE).

Depending on the nature of the central metal, the oxygen reduction could take place via four-electron reduction to water (iron complexes), two-electron reduction to H₂O₂ (cobalt complexes) or other pathways somewhere within this range. The central metal ion of the macrocycle seemed to play a decisive role in the oxygen reduction mechanism. For N₄-chelates (phthalocyanines) the influence of the metal ion was displayed in the following order of activities [66]



Alt et al. [68] explained this sequence of activity by molecular orbital (MO) theory based on oxygen adsorption. According to this model, the back bonding of filled d_{xz} and d_{yz} orbitals and empty d_{z²} orbitals favours the partial electron transition from the metal to the empty, or partially filled π* orbitals of oxygen. Although iron complexes of phthalocyanine/porphyrin can promote a four-electron reduction pathway, they are not stable. In general, cobalt complexes have higher electrochemical stability than that of iron, but they can only catalyze a two-electron reduction of oxygen. The following stability sequence of metal macrocyclic complexes was summarized [69]



In order to combine the advantage of Fe complex four-electron O₂ reduction with the higher electrochemical stability of Co complexes, Chu et al. [70] studied the effect of the heat-treated mixture of two transition metalloporphyrins (V/Fe, Co/Fe, Ni/Fe or Cu/Fe) on oxygen reduction and compared it with that of heat-treated single transition metalloporphyrin. They found that the heat-treated mixture of Fe and Co tetraphenylporphyrins could give a much higher catalyzed oxygen reduction current than that of single Fe tetraphenylporphyrin or Co tetraphenylporphyrin. This could be attributed to the formation of a face-to-face structure with two kinds of metal active sites, as suggested by Anson et al. [71,72]. The interaction between two different transition metals and oxygen molecules could promote the O–O bond breakage and cause an easier reaction to H₂O. The N₄-chelate ligand could also play an important role in oxygen reduction. In addition to serving as part of the active site, it kept the metal in a stable form on the electrode surface. Tetraphenylporphyrin, tetramethoxyphenylporphyrin, dibenzotetraazaannulene, and phthalocyanine, all of which can form complexes with iron and cobalt, seemed to be favourable in forming catalysts. Even so, when these complexes were used in PEM fuel cells, they could not show enough chemical/electrochemical stability when compared with Pt based catalysts. For example, the Fe phthalocyanine stability weakened due to disintegration at a temperature above 50 °C in an acid electrolyte [73]. In order to improve the stability of these complexes, an attempt to enlarge the organic part of the molecule and to make a stronger attachment to the support base was undertaken, but the results were not promising [74].

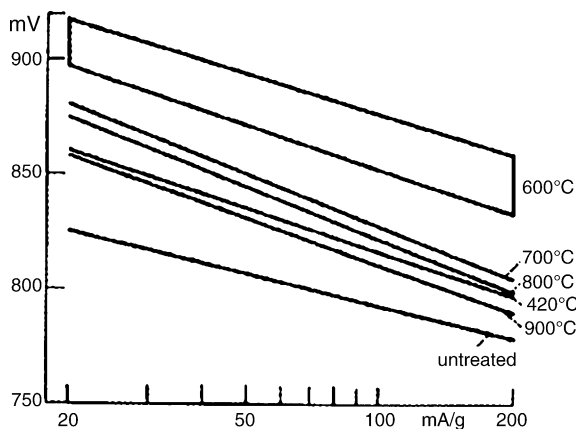


Fig. 6. Dependence of thermal activation on temperature of CoTAA (Electrolyte: 4.5 N H₂SO₄) [23].

In 1976, Jahnke et al. [23] reported that the heat-treatment of metal N₄-chelates at high temperature could remarkably increase the catalyst activity and stability toward oxygen electroreduction. Since then, this pioneering work has led to a worldwide research interest. Fig. 6 shows the influence of heat-treatment on CoTAA (Co Dihydrodibenzotetraazaannulene) catalysis activity. According to Jahnke et al., thermally pretreated 1:2 (w/w) mixtures of CoTAA and activated carbon BRX showed the maximum activity at a temperature of 600 °C for oxygen reduction [23].

Some recent research [75–77] revealed that the highest level of activity for N₄-chelates could be obtained at a pyrolysis temperature range of 500–700 °C. However, it was also discovered that a higher pyrolysis temperature (>800 °C) was necessary in order to obtain a stable performance in PEM fuel cells as shown in Fig. 7 [76].

However, a deleterious effect on the electrode performance was observed at temperatures higher than 1100 °C [78]. An almost 50 times greater enhancement in the electrocatalytic activity was achieved at an electrode potential of 700 mV (versus NHE) when carbon-supported Co phthalocyanine was heat-treated in an environment of N₂ or Ar at 700–800 °C [79]. Even for carbon-supported Fe phthalocyanine, the stability was also improved considerably. In experiments with carbon-supported Ru phthalocyanine, heat treatment at 650 °C could increase catalytic activity by 20 times at 800 mV (versus NHE), but stability was not improved. Not all carbon-supported metal phthalocyanines produced positive results to heat treatment. For example, the activity and stability of Zn- and Mn-phthalocyanines were not affected by heat treatment [79]. The duration of heat-treatment for these complexes was usually around 0.3–5 h.

When heat treatment was performed at a lower temperature range (500–700 °C), N₄-M moiety was recognized as the active catalytic site. However, at a higher temperature range (i.e., >800 °C), the nature of the catalytic site of high temperature pyrolysis products is still controversial. According to some research [80–82], the N₄-metal super-site disappeared when the temperature was too high, suggesting that

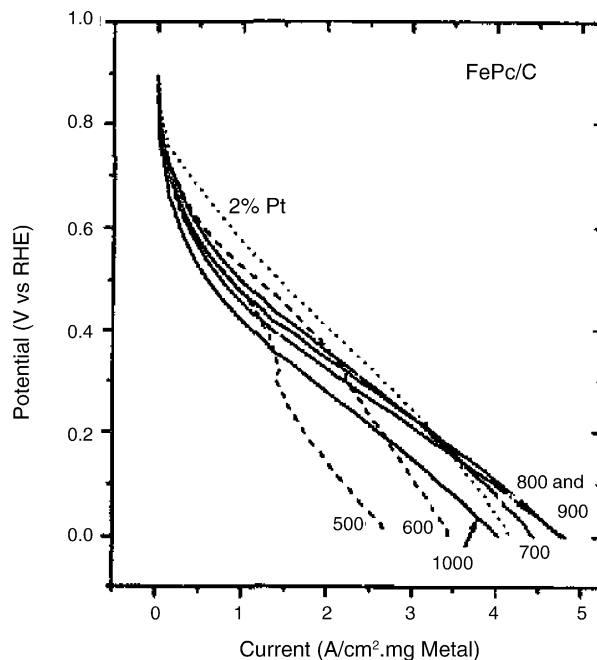


Fig. 7. Polarization curves, reordered at 50 °C, for the catalysts obtained after the heat-treatment of FePc/C at various temperatures: (—) stable catalysts; (---) unstable catalysts, and (...) 2 wt.% Pt/C catalyst [76].

the nature of such active sites was changed due to the higher temperature hydrolysis process. In researching catalytic sites produced at high temperature, Dodelet et al. [83] investigated the activity and active site of Fe precursors. Dodelet used Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), through pyrolysis of perylene tetracarboxylic dianhydride (PTCDA) together with Fe and N precursors. The only species detected in the results was FeN₂C₄⁺. Therefore, it was proposed that FeN₂C₄⁺ might be a catalytic site that is produced in the high temperature range.

Since the structure of these N₄-chelate catalysts would be largely destroyed at high pyrolysis temperatures, it might not be necessary to use expensive metal macrocyclic complexes as precursors for active catalyst preparation [84]. It was expected that if a mixture of basic components from macrocyclic complexes, i.e., transition metal sources, such as Fe, or Co, nitrogen donors and carbon supports could be treated at a high temperature, active catalytic sites such as N₄-metal or FeN₂C₄⁺ might be obtained [85]. Several research groups have reported their work on this alternative preparation route with various transition metal, nitrogen and carbon containing species as precursors. This approach created a very attractive means of electrocatalyst preparation using more popular starting materials that were much cheaper. In general, the most popular transition metal precursors that have been employed are Fe or Co inorganic salts, such as sulphates, acetates, hydroxides, chlorides, cyanides, [86–88] and Fe complexes such as ferrocene [89]. Inorganic precursors would be more economical for commercialization. The complex of Fe-, Co- or Cu-1,10-phenanthroline has been widely employed as a precursor for catalyst preparation

[16,37,77,90] due to coordinated bonds between the metal ion and the nitrogen ligand which appeared to be critical to the formation of active catalyst sites such as $\text{MeN}_4/\text{or FeN}_2\text{C}_4^+$ after heat treatment.

Nitrogen sources were critical to catalytic activity. Nitrogen-containing chemicals such as polyacrylonitrile, tetracyanoquinodimethane, ethylenediamine, 1,2-phenylenediamine, hydrogen phthalocyanine, pyrrole and their derivatives have been found to be the effective precursors for catalyst preparation [87,91,92]. N-containing gases such as NH_3 [93] or acetonitrile [94], and N groups on a modified carbon support (e.g., HNO_3/NH_3 treated carbon support [95]) were also employed as the nitrogen sources for the preparation process. It was clear that the most important factor was the nitrogen content of the materials. Higher nitrogen content yielded higher catalytic surface site density, and better electrocatalysts [96].

Carbon support was another factor affecting catalytic activity. Jaouen et al. [96] studied the effect of carbon support on catalytic activity and found that the activity of the catalyst varied with the specific surface area, pore size distribution, and the N or O content of the carbon support.

Metal loading on the carbon support may also affect catalytic activity. Lalande et al. [30] studied the influence of transition metal Co loading (0–8 wt.%) on the activity and stability of heat-treated carbon-supported Co phthalocyanine at a temperature range of 500–1100 °C. They found an optimum value for Co loading on the carbon support (~3.5 wt.%). This optimum Co loading did not appear to depend on the heat treatment temperature. They also found that this optimum Co loading value corresponded to full monolayer coverage of the Co phthalocyanine on the carbon support. Faubert et al. [97] also studied the effect of Fe loading on catalytic activity by heating PTCDA that was adsorbed by Fe acetate in an environment of $\text{Ar} + \text{H}_2 + \text{NH}_3$. It was found that the catalytic activity at first increased with an increase in Fe content, but levelled off when Fe content was greater than 0.5 wt.%. This result suggested that excess Fe would favour the formation of aggregates, which contained catalytic inert metallic and/or carbidic iron.

Lalande et al. [89] proposed a multi-step pyrolysis method for O_2 reduction catalyst preparation. Wei et al. [94] did some comparisons between the carbon, nitrogen and cobalt contained catalysts prepared by one-step pyrolysis and those prepared by multi-step pyrolysis methods. In the multi-step pyrolysis method, the first pyrolysis step was to pyrolyze the carbon support (Vulcan XC-72R) with a nitrogen precursor (acetonitrile) in a flowing argon atmosphere, and then to introduce the cobalt precursor (cobalt sulphate) into the reactor for the second step. The second step was to pyrolyze the mixture of the product from the first step and the introduced cobalt precursor in a flowing argon atmosphere. The pyrolysis sequence was found to have a strong impact on the catalyst activity. However, the onset electrode potential for electrocatalyzed oxygen reduction (E_{onset}) for catalysts that were produced in different pyrolyzation sequences were

Table 2
Preparation methods for Fe and Co heat-treated catalysts for Oxygen electroreduction

Methods	Starting chemicals	Operating environment	Possible catalysts produced	Catalytic activity (E_{onset}) ^a	O_2R reduction	Refs.
Pyrolyzed N_4 -metal macrocycles	Fe or Co N_4 -macrocycles	Pyrolyzed at ~1000 °C, with carbon support in argon	CoPc/C	~800 mV (vs. RHE)		[98,99]
Single-step method	Independent Fe or Co precursors, N and C sources	Pyrolyzed at ~1000 °C in argon	CNCo	790–800 mV (vs. RHE)		[94]
Multi-step method	Independent Fe or Co precursors, N and C sources	Pyrolyzed at ~1000 °C in argon	CNCo	790–800 mV (vs. RHE)		[94]
Sol-gel method	Independent Fe or Co precursors, N and C sources	DMF/water solvent, pyrolyzed at 900 °C in argon	PAN-Co or PAN-Fe	0.60 V for PAN-Fe, 0.55 V for PAN-Co and 0.71 V (vs. NHE) for Pt at maximum current.		[100]

^a The potential at which the cathodic current for oxygen reduction is first observed.

all produced at about 790–800 mV (versus RHE), similar to that obtained with cobalt-centred macrocycle compounds pyrolyzed at 1000 °C [98,99].

More recently, Ye et al. [100] proposed a new sol–gel method combined with a supercritical drying technique for the preparation of nanocomposite electrocatalysts for oxygen reduction. They claimed that a sol–gel method using a highly controllable solution, plus a supercritical drying technique with structure-preserving ability could favour a nanoscale mixing of the constituents to produce a remarkably homogeneous solution. Chemical, physical and morphological properties of the products of this sol–gel method could have a pronounced isotropy. Compared to other preparation methods, this new sol–gel method had some unique and competitive features. The first step for this synthesis method was the mixing of inorganic salt (e.g., $\text{Fe}(\text{NO}_3)_3$ or CoCl_2) or an organometallic compound (e.g., Co(III) acetylacetonate) with polyacrylonitrile (PAN) in *N,N*-dimethylformamide (DMF)/water to form a well-mixed solution. The mixed solution was degassed when heated to approximately 120 °C. When the solution cooled, a polymer gel containing the metallic compound was obtained by thermally induced phase separation. The polymer gel was then pretreated at 220 °C, followed by a pyrolysis step at 900 °C under an argon atmosphere. In this way, a non-noble catalyst was produced which showed strong catalytic activity for oxygen reduction in acid conditions and a relatively high stability.

For the purposes of comparison, Table 2 lists all methods employed for the preparation of Fe and Co heat-treated electrocatalysts and their corresponding electrocatalytic activities towards oxygen reduction.

Finally, it is worthwhile to mention that the catalyst layer structure also has a significant impact on catalyst performance. For example, if the preparation procedure for an electrode catalyst layer is changed, which could result in a different catalyst layer structure, the cathode catalytic activity could also be different. Elzing et al. [101] reviewed the influence of electrode preparation methods on oxygen reduction electrocatalysis in both acid and alkaline conditions by employing Co phthalocyanine catalysts. Five different preparation methods were compared. These were: (a) irreversible adsorption; (b) vacuum deposition; (c) incorporation in polypyrrole; (d) impregnation of porous carbon; (e) evaporation of the solvent. It was concluded that (1) the vacuum-deposited layer had a lower activity than that of the irreversibly adsorbed layer; (2) the electrode obtained by evaporation of the solvent showed a slightly higher activity than that of the vacuum-deposition method; and (3) the method of incorporation in polypyrrole had the best catalytic activity for oxygen reduction in an acid medium.

4. Conclusions

Much effort has been made to discover non-noble oxygen reduction electrocatalysts that are stable and show strong

catalytic activity. Various catalyst preparation methods have been developed. In recent years, fuel cell commercialization has driven extensive research and development in this area. Although no breakthroughs have been made yet, great progress has been made, especially in the area of catalyst synthesis methods. Through effective catalyst synthesis procedures, new non-noble catalysts have been discovered. Transition metal chalcogenides, mainly carbon-supported Ru-based sulfides and selenides, and heat-treated carbon-supported Fe or Co nitrogen containing macrocyclic complexes show promise. Unfortunately, neither of these catalyst groups has reached the level of a Pt based catalyst in terms of catalytic activity, durability and chemical/electrochemical stability. Much more research is needed to produce commercially valid non-noble electrocatalysts.

It is worthwhile to point out that Ru-based chalcogenides may not be real non-noble catalysts because ruthenium is actually a noble metal, which is also very expensive.

Several points may be suggested:

- (1) Cost-effective and innovative catalyst synthesis methods are necessary for new catalyst discovery and catalyst performance optimization.
- (2) Carbon support functionality should be emphasized in terms of the catalyst active surface increase, the coordination effect of catalyst and support, and the distribution of active catalytic sites. For example, carbon nano-tube supported catalysts may have a potential to improve performance.
- (3) Mo metal may not be a necessary component for amorphous chalcogenide catalysts ($\text{Ru}_x\text{Mo}_y\text{Se}_z$). This has been confirmed by the observation that when Ru_xSe binary chalcogenide catalysts are used, comparable electrocatalytic activity for oxygen reduction was obtained.
- (4) Research shows that simple organic/inorganic metal salts and nitrogen containing chemicals produce active catalysts. It may not be necessary to use expensive metal macrocyclic complexes for heat-treated Fe and CO catalyst synthesis.

Acknowledgement

We wish to thank the Institute for Fuel Cell Innovation, National Research Council Canada (NRC-IFCI) for its financial support. The proof reading by Mrs. Nancy Glass of NRC-IFCI is highly appreciated.

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