Canadian nuclear hydrogen R&D programme: Development of the medium-temperature Cu-Cl cycle and contributions to the high-temperature sulphur-iodine cycle

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Abstract

Canada is developing the heavy-water-moderated supercritical water reactor as its Generation IV nuclear system. The medium temperature copper-chlorine (Cu-Cl) cycle has been selected as a suitable process for integration with this reactor system for large-scale production of hydrogen. A collaborative programme uniting the University of Ontario Institute of Technology (UOIT), Argonne National Laboratory (ANL) and Atomic Energy of Canada Limited (AECL) is underway for the development of the complete cycle for pilot plant demonstration. Canada's Generation IV National Programme also supports the international efforts on VHTR through R&D on areas that are synergistic with the Canadian efforts on SCWR. Some of the latest results in the development of the Cu-Cl cycle and Canada's contributions to the sulphur-iodine cycle are described in this paper.

Introduction

Canada has been a very successful nuclear vendor country with its CANDU reactors placed among the best performing ones across the world. With the largest known high-grade uranium deposits located in the Province of Saskatchewan, Canada also enjoys the benefits of being one of the top suppliers of uranium in the world. Currently, there are 22 CANDU reactors in Canada (located in three provinces), and 12 Canadian-designed CANDU reactors outside of Canada in 6 countries (AECL, 2006-2008). Nuclear energy accounts for approximately 15% of Canada's total electricity and 51% of the Province of Ontario's electricity production in 2007 (CNA, 2008).

In 2006, Natural Resources Canada (NRCan) established a national programme (Generation IV National Programme) to support Generation IV research and development specifically relevant to Canada and to meet Canada's commitments to Generation IV Forum (GIF) (Brady, 2007). NRCan is the department in the federal government of Canada responsible for establishing policies, priorities and programmes for energy science and technology (S&T). Canada's Generation IV National Programme focuses on developing a Super-critical Water-cooled Reactor (SCWR). Canada's development of the SCWR as its next generation reactor is firmly based on the current experience with pressure-tube, heavy-water-moderated CANDU reactors. While focused on SCWR, Canada's Generation IV National Programme also supports the international efforts on VHTR through R&D on areas that are synergistic with the Canadian efforts related to SCWR. The medium-temperature (<550°C) copper-chlorine thermochemical cycle is being developed for integration with the SCWR for hydrogen production. Adaptation of the high-temperature (>800°C) sulphur-iodine (S-I) thermochemical cycle to suit the lower temperature (<625°C) of the SCWR is also being investigated.

Cu-Cl cycle developments

The Cu-Cl cycle [Eqs. (1-4) in Table 1] has been identified by AECL, in agreement with the Argonne National Laboratory (ANL), as the most promising thermochemical cycle for hydrogen production suitable for integration with Canada's SCWR designs. This moderate temperature cycle consists of three thermal reactions for generating H_2, O_2, and HCl [Eqs. (1), (3) and (4)] and one electrochemical reaction [Eq. (2)]. Since ANL has been involved in the development of this cycle over several years, AECL initiated a collaborative development programme with them about three years ago. Around the same time, the University of Ontario Institute of Technology (UOIT), Ontario, Canada, adopted nuclear energy as one of their main strategic research fields for concentration. As a result, they have established a Nuclear Engineering Programme in the School of Energy Systems and Nuclear Science. In collaboration with several other universities (University of Waterloo, University of Guelph, University of Western Ontario, University Maribor, etc.), research organisations (ANL) and AECL, they have initiated a nuclear hydrogen programme. Because of its relevance to Canada's SCWR programme, UOIT has chosen the Cu-Cl cycle development for nuclear hydrogen production. UOIT has now established an overarching programme covering all aspects of the development of the Cu-Cl cycle. AECL supports this programme through financial and technical contributions. Because of its expertise in the fields of electrolysis, AECL's technical contribution is focused on the development of electrochemical aspects involved in the cycle.

**Table 1: Reactions involved in the Cu-Cl cycle – four-reaction option**

Equation	Reaction stoichiometry	Temperature (°C)	Remarks
1	$2Cu + 2HCl(g) \rightarrow 2\ CuCl(l) + H_2(g)$	425-450	Thermal
2	$4CuCl(a) \rightarrow 2CuCl_2(a) + 2Cu$	< 100	Electrochemical
3	$2CuCl_2(s) + H_2O(g) \rightarrow Cu_2OCl_2\ (s) + 2HCl(g)$	300-375	Hydrolysis
4	$Cu_2OCl_2\ (s) \rightarrow 2CuCl(l) + \tfrac{1}{2}O_2(g)$	450-530	Thermal

Following further research into the development of the Cu-Cl cycle, AECL proposed a variant of the cycle (Dokiya, 1976) involving direct generation of hydrogen through the following electrochemical step, Eq. (5), replacing steps shown in Eqs. (1) and (2) in Table 1, simplifying the process in a significant way.

$$2CuCl + 2HCl \rightarrow H_2 + CuCla_2 \qquad < 100°C \qquad\qquad (5)$$
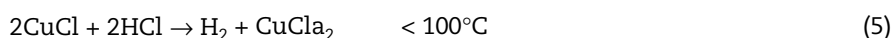
The work being carried out at AECL is mainly focused on the development of an electrolysis cell to carry out the step shown in Eq. (5). Figure 1 shows the flow diagram of the single-cell electrolysis test facility used for this development. The catholyte, 6 M HCl, is held in a modified 4 L volumetric flask labelled "Catholyte Reservoir". A peristaltic pump is used to pump the 6 M HCl solution from the reservoir to the two ion exchange columns. The first ion-exchange column, containing DOWEXTM 21K XLT anion exchange resin, removes copper(II) chloride complexes. The second ion exchange column, containing DOWEXTM M4195, a chelating ion exchange resin, removes uncomplexed copper(II) cations. Following the two ion exchange columns, the catholyte passes through the cathode compartment of the electrolysis cell and then returns to the catholyte reservoir for recycling.

Figure 1: Experimental set-up used for single-cell electrolysis experiments
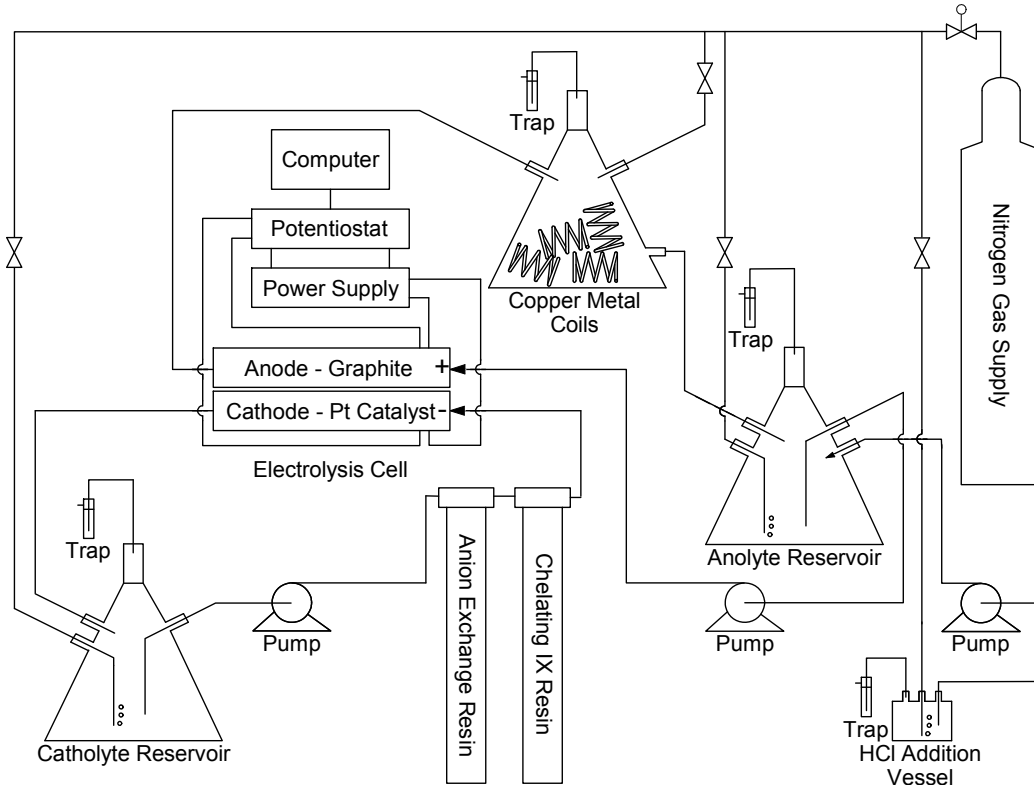
The anolyte, typically 1.0 M CuCl in 6 M HCl, is also held in a modified 4 L volumetric flask labelled "Anolyte Reservoir". In the anode compartment, copper(I) is oxidised to copper(II). After the anolyte leaves the anode compartment, it enters a modified 2 L volumetric flask that contains copper metal coils. Copper(II) that is present in the anolyte reacts with the copper metal to give two moles of Cu+ for every mole of Cu2+ that enters the flask. The anolyte solution then returns to the anolyte reservoir and is recycled. Because the reaction between Cu2+ and copper metal increases the Cu+ concentration, 6 M HCl is added to the anolyte reservoir to maintain the Cu+ concentration at a relatively constant value. The HCl solution required for this purpose comes from the "HCl Addition Vessel".

The voltage or current is applied across the electrolysis cell using the "Potentiostat" and "Power Supply". This instrumentation is controlled by the "Computer", which also collects and stores experimental data.

A commercially available fuel cell (Figure 2) was used for the initial work with low-flow experiments and a custom-made cell (Figure 3) was used for the high-flow experiments.

When the low-flow rate single-cell electrolysis cell was used the cathode and anode were fabricated by painting one side of a 5 cm^2 piece of EC-TP1-060 Toray Carbon Fiber Paper with Pt on XC-72R catalyst mixture. In high-flow rate single-cell electrolysis experiments the cathode was a

**Figure 2: Photograph of the single-cell commercial fuel
cell used for low flow CuCl/HCl electrolysis experiments**

**Figure 3: Photograph of the custom-made high flow single-cell electrolysis cell**

Pt/XC-72R catalyst mixture that was sprayed directly onto one of the graphite separator plates that came with the high-flow rate single-cell electrolysis cell. We have found that the copper(I) oxidation reaction does not require a catalyst (see below). Thus, a catalyst-free graphite separator plate was used as the anode. Nafion membranes were used as the electrolyte for H+ conduction.

The polarisation curves presented in Figure 4 for the copper(I) oxidation reaction show that they tend to merge with one another when the electrode potential is < 0.25 V (SCE). In this region the kinetics of the electrode reaction is controlled by the electron transfer reaction that takes place at the electrode surface. Under this condition, the current density does not show a dependence on the nature of the substrate or on the absence or presence of a platinum catalyst. When the electrode potential is > 0.4 V (SCE) the kinetics of the electrode reaction is controlled by mass transfer. In this case, the current density displays a strong dependence on both the substrate and on the absence or presence of a platinum catalyst. In the region where the electrode kinetics is under mass transfer-control, higher current densities are observed for working electrodes fabricated from a graphite separator plate. For a given substrate, higher current densities are generally observed for catalyst-free working electrodes. The highest current densities are observed with a catalyst free GSP.

The results from Figure 4 show that a catalyst like Pt is not required to carry out the copper(I) oxidation reaction. Thus, the anode of a single-cell electrolysis cell can be a Pt-free graphite separator plate. A Pt-free anode will reduce the capital cost of a large-scale commercial electrolyser quite significantly.

**Figure 4: Half-cell polarisation curves for the copper(I)
oxidation reaction at the indicated working electrodes**
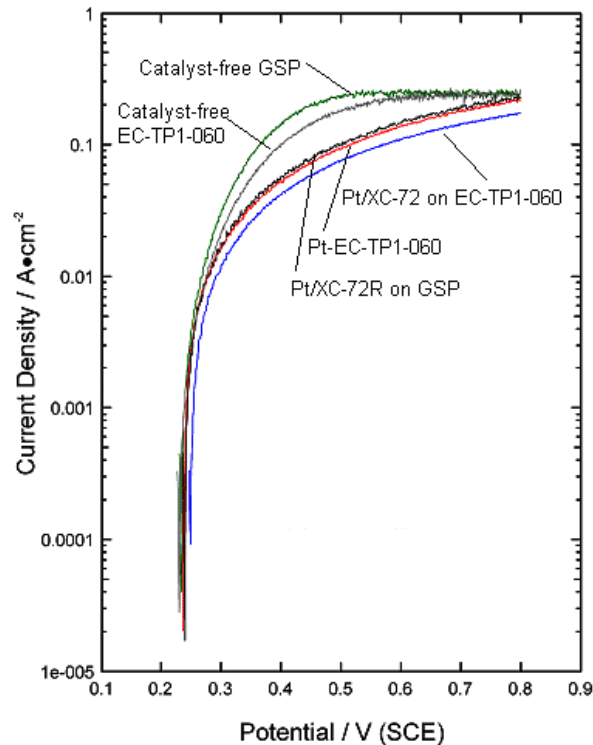
The polarisation curves obtained for the hydrogen production reaction are presented in Figure 5 with the working electrodes indicated on the figure. As the data shows, very small current densities are observed from the Pt-free working electrodes. This confirms that a catalyst is required to carry out the hydrogen production reaction. The other three polarisation curves presented in Figure 5 were obtained from working electrodes that incorporate a platinum catalyst. As the data shows, the largest current densities are observed from a working electrode that was fabricated from a graphite separator plate and painted with a Pt/XC-72R catalyst mixture.

The polarisation curve shown in Figure 6 describes the kinetics of the single-cell CuCl/HCl electrolysis reaction over the potential region indicated on the figure. As this data shows, the CuCl/HCl single-cell electrolysis reaction is under mass transfer control in the potential region 0.5 V to 0.9 V. This means that the current densities in this region are dependent upon the flow rate of the anolyte and/or catholyte solution through their respective compartments. At 0.9 V, 0.8 V and 0.7 V the current density was found to be 0.429 A·cm^{-2}, 0.342 A·cm^{-2} and 0.238 A·cm^{-2}, respectively.

During the development of the CuCl/HCl electrolysis reaction three recurring issues have been identified which can be summarised as follows:

1) The equilibrium potential of the single-cell electrolysis cell, as determined from polarisation curves, increases during single-cell electrolysis experiments.

2) Copper ions, presumably copper(II), enter the catholyte solution from the anolyte solution by crossing the membrane during electrolysis experiments.

3) During most constant current half-cell electrochemical experiments the working electrode potential for the hydrogen production reaction increases with time.

The first issue identified above has been solved while the other two are presently being addressed. In order to get meaningful experimental data, and to further develop the CuCl/HCl electrolysis reaction, all of these issues need to be resolved. Some of these issues are artefacts of the way in which the electrolysis reaction is being carried out in the laboratory (Issue #1) while others are related more

Figure 5: Half-cell polarisation curves for the hydrogen production reaction on the indicated working electrodes
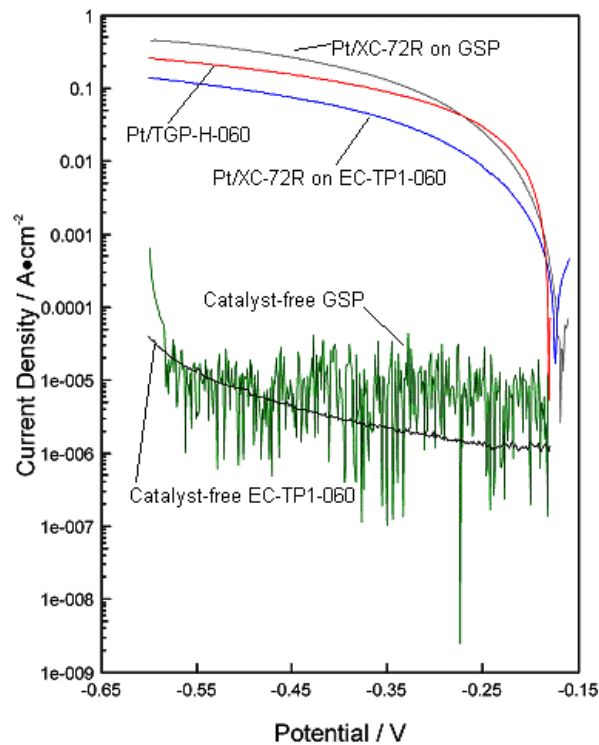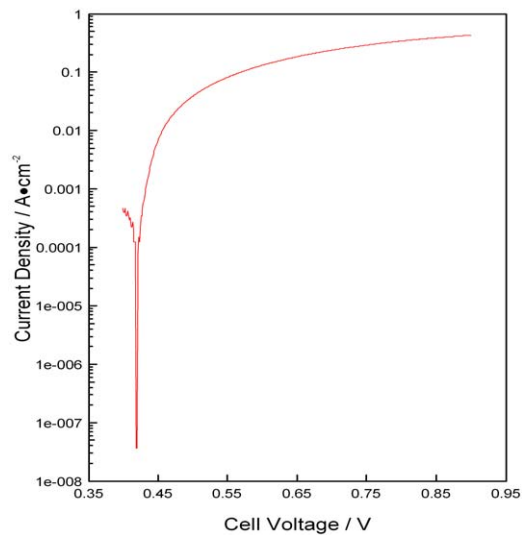

Figure 6: Single-cell polarisation curve

to process development (Issue #3). To some extent, Issue #2 is also an artefact; however, one goal of process development is to develop membranes that do not allow copper ions to cross over from the anolyte solution to the catholyte solution. In a few single-cell electrolysis experiments, copper metal was visually observed on the cathode (Figure 7) when the cell was disassembled at the completion of the test.

Figure 7: Copper deposits formed on the cathode
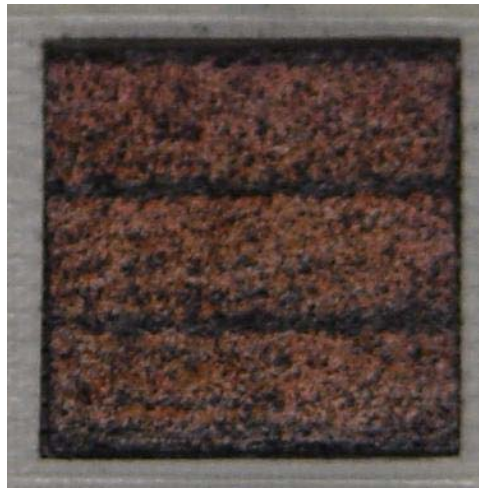
Sulphur-iodine cycle

The sulphur-iodine (S-I) cycle (Table 2), originally developed by General Atomics, is considered to be one of the best thermochemical hydrogen production processes currently under development in many countries. While the very high temperature reactors (VHTR) being developed in many countries, including the USA and Japan, are capable of satisfying the high temperature requirements of all the steps of this process, Canada's SCWR can satisfy the temperature requirements of all but the catalytic SO_3 decomposition step. However, AECL's direct electrically heated catalytic structures (Spagnolo, 1992) may be used for the decomposition with only a marginal lowering of the overall efficiency of the S-I process. An experimental programme has been ongoing to investigate the use of these structures containing Pt or Fe_2O_3 as catalyst for the decomposition over the temperature range of 500 to 1 000°C. While the main objective is to measure the decomposition rate and its dependence on temperature, great effort is focused on identifying suitable materials for the metal structure used for direct heating under the extreme corrosive conditions of the decomposition process. The catalytic decomposition rates are required for the optimisation of the process and estimation of realistic capital costs.

**Table 2: The steps involved in the sulphur-iodine cycle**

Reaction	Temperature (°C)	Remarks
$I_{2(l)} + SO_{2(g)} + H_2O_{(l)} \rightarrow 2HI_{(aq)} + H_2SO_{4(aq)}$	~120	Bunsen reaction
$H_2SO_{4(g)} \rightarrow SO_{3(g)} + H_2O_{(g)}$	<500	Sulphuric acid decomposition
$SO_{3(g)} \rightarrow SO_{2(g)} + 0.5O_{2(g)}$	>800	Sulphur trioxide decomposition
$2HI_{(g)} \rightarrow I_{2(g)} + H_{2(g)}$	~425	Hydrogen iodide decomposition

A schematic of the experimental test rig used to study the performance of electro-resistively heated catalysts is shown in Figure 8. The test rig includes a direct electro-resistive heating reactor (Hastelloy C-276) containing the catalyst. Concentrated H_2SO_4 is introduced to the reactor and heated to 500~550°C in a pre-heating section to decompose it into SO_3 and H_2O vapour. N_2 gas is used as the carrier gas to blow the decomposition products through the reactor. SO_3 decomposition takes place on the catalyst to produce gaseous SO_2 and O_2. Following SO_3 decomposition, the gaseous products pass through a condenser cooled by water at 1°C, three bubblers containing 5%, 15% and 30% potassium hydroxide, respectively, to absorb acidic components in the gaseous products, an empty ice/dry-ice cooled container used as a thermal buffer, a gas conditioning unit to capture acidic gas residues, and an oxygen analyser.

Figure 8: Schematic of the electro-thermal SO$_3$ decomposition test apparatus
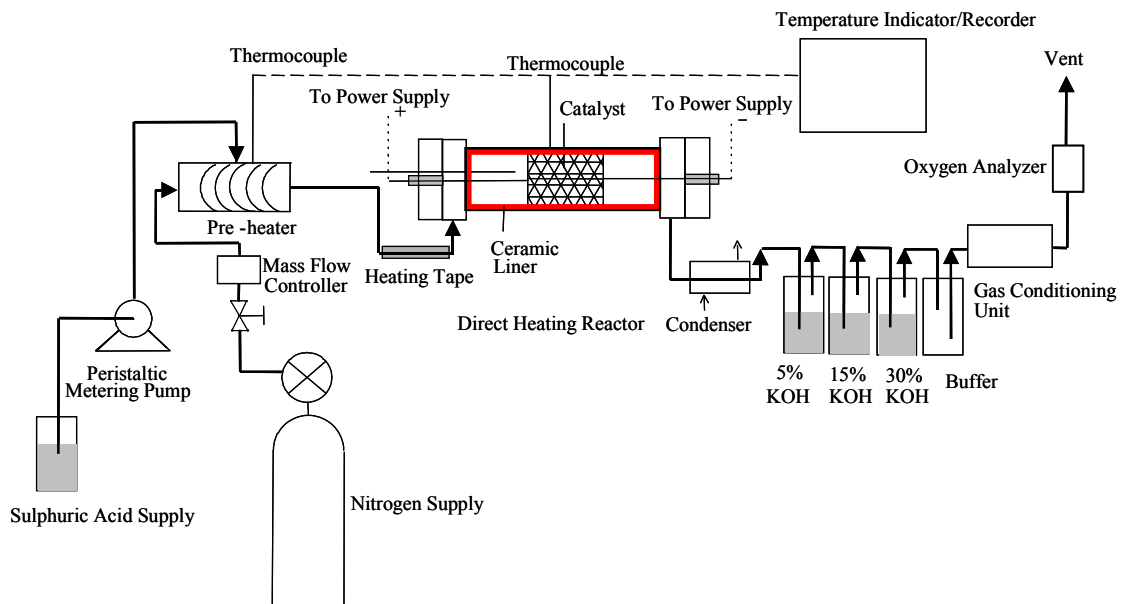
For the tests discussed in this paper, the N$_2$ gas flow rate was maintained at 700 or 1 100 mL·min^{-1} and the concentrated H$_2$SO$_4$ acid was added to the system at a rate of 0.06 to 0.17 mL·min^{-1} at room temperature. This produced a H$_2$SO$_4$ concentration of 3 to 6% in the N$_2$ gas at the inlet of the SO$_3$ decomposition reactor.

Figure 9 shows a photograph of the catalyst coated metal strips used for the decomposition reaction.

Figure 9: Catalyst strips: Hastelloy strips coated with Pt/TiO$_2$ or Fe$_2$O$_3$ catalyst
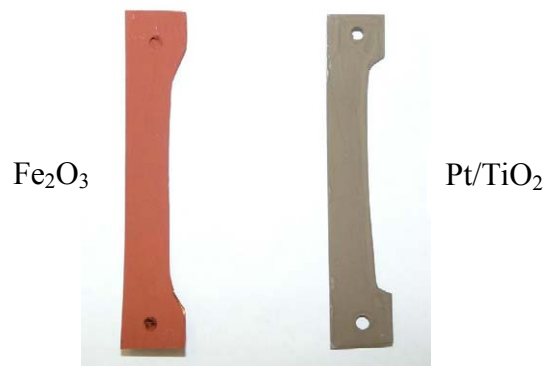
A comparison of the results in Figures 10 and 11 show that Pt-TiO$_2$ is an active catalyst even at temperatures as low as 550°C while the Fe$_2$O$_3$ catalyst is active only at temperatures above 600°C. The SO$_3$ conversion reached 53% and 40% at 800°C with 10% Pt/TiO$_2$ and Fe$_2$O$_3$ catalysts, respectively. Platinum supported on TiO$_2$ has been singled out as one of the best catalysts for this decomposition though its cost may be a significant deterrent for its application. However, since the fraction of Pt cost in the catalyst structure is expected to be small in comparison with the complete decomposer, we propose to consider Pt-based catalyst structures in depth. On the other hand, Fe$_2$O$_3$ is considered to be a more cost-effective catalyst with a moderately high activity, and Fe$_2$O$_3$ forms an excellent coating on the metal structures. At AECL, both these catalysts are being considered for electro-resistive heating.

Figure 10: SO$_3$ conversion with Pt/TiO$_2$ catalyst coated on Hastelloy strip
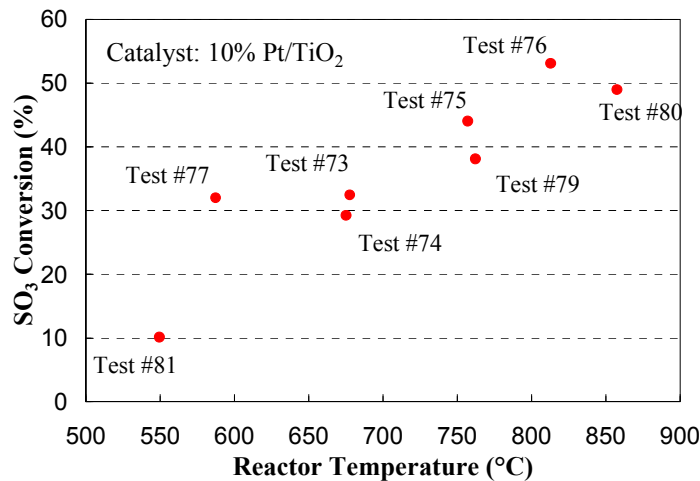
Figure 11: SO$_3$ conversion with Fe$_2$O$_3$ catalyst coated on Hastelloy strip
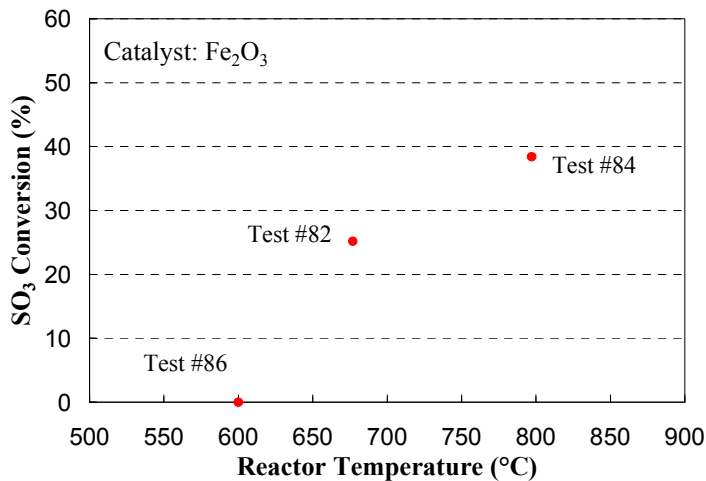
Conclusions

The Canadian Generation IV National Programme has helped to establish a comprehensive R&D programme on nuclear hydrogen production. This programme maximises the benefit to Canada and supports the international collaboration.

The experimental data presented in this paper demonstrates the potential of CuCl/HCl electrolysis for nuclear hydrogen production. The CuCl/HCl electrolysis reaction requires a cation exchange membrane in order to produce hydrogen at a current density that exceeds 0.1 A·cm^{-2}. In order to carry out the hydrogen production reaction a platinum electro-catalyst is required. The copper(I) oxidation reaction, on the other hand, does not require a Pt catalyst. This reaction proceeds quite readily on Pt-free graphite electrodes. Methods to mitigate the passage of the copper ion species across the membrane need to be developed to maintain the performance of the cell at the desired level.

Electro-resistively heated Pt-TiO$_2$ or Fe$_2$O$_3$ catalysts supported on Hastelloy C-276 have been successfully used for the decomposition of SO$_3$. The Pt-TiO$_2$ catalyst has been shown to be active over a wider range of temperatures compared to the Fe$_2$O$_3$ catalyst. The combination of these two catalysts with electro-resistive heating may offer a novel method for SO$_3$ decomposition in the S-I process.
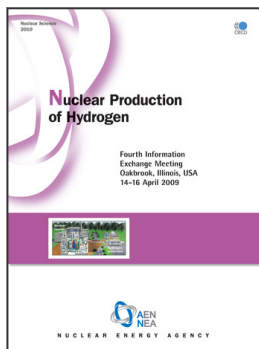
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