RMIT University Melbourne Hydrogen Storage and Transport R & D Project:

A proton flow reactor system for electrical energy storage and bulk export of hydrogenated carbon-based material

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Public Midterm Activity Report

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Disclaimer

Acronyms and abbreviations

aC: activated carbon

ANSYS: trade name of a computer simulation software package

C: carbon

H: hydrogen

I2CNER: International Institute for Carbon Neutral Energy Research

IP: intellectual property

M: molar

Matlab: trade name of a mathematical solution and simulation software

O: oxygen

PR: phenolic resin

sp^2, sp^3: forms of hybridisation of electronic orbitals, by combining s and p orbitals in various linear combinations

V: volt

wt: weight

1 Introduction

This report is the Public Mid-Term Activity Report for the RMIT University Melbourne Hydrogen Storage and Transport R & D Project, entitled “A proton flow reactor system for electrical energy storage and bulk export of hydrogenated carbon-based material”, covering:

- Project summary (section 2)
- Progress update, including key highlights and difficulties (section 3)
- Commentary on commercialisation prospects (section 4)
- Knowledge-sharing activities completed (section 5).

The report is open for public distribution and contains no commercially-confidential information.

2 Project summary

The aim of this project is to develop an integrated system for storage of electricity from renewable energy and export the stored energy as hydrogen within hydrogenated carbon-based material. The project commenced in August 2018, and reached its second milestone on 1 July 2020. This summary presents progress up to this date.

A novel ‘proton flow reactor’ system for producing hydrogenated carbon(C)-based powder for bulk export is being developed. This reactor – a novel and scaled-up extension of RMIT’s innovative proton battery concept – will use electricity from renewables to split water and charge a stream of C-particles in a slurry electrode with the protons produced.

This system offers a zero-emission and environmentally-benign solution to production of exportable hydrogenated material from renewable energy and abundant carbon primary sources for conversion to electricity overseas. It may also store intermittent renewable energy on electricity grids at various scales.

RMIT’s industry partner in this project is Eldor Corporation, Italy; and the International Institute for Carbon Neutral Energy Research and Kyushu University in Japan are academic research partners.

3 Progress update

The main deliverable in milestone 2 was a technical proof-of-concept of the proton flow reactor system, including experimental demonstration of the technical feasibility of the main components of the proton flow reactor system. These are the proton flow reactor itself operating in charge and discharge modes, and the storage of hydrogen over time in C-particles with the liquid electrolyte used to charge them with hydrogen removed.

The principal evidence obtained to date that the proton flow reactor system concept is technically feasible is threefold:

A. The system has been experimentally demonstrated in a proton reactor with a paste electrode

The paste electrode was made by mixing activated carbon from phenolic resin particles in a 1 M sulphuric acid electrolyte. It is thus a limiting case of a slurry electrode with a near maximum density of suspended particles. The paste electrode was charged with hydrogen in a proton battery/reactor specially designed for this form of electrode.

The paste electrode was then dried by blowing argon through it so that it returned to near powder consistency. It was left in the dried state for nearly a day. Acid electrolyte was then added again to return the electrode to a paste, and the proton battery/reactor was discharged to produce electricity.

Measurements of the integrated charge flow showed that around 60% of the hydrogen stored in the electrode after charging was recovered. Allowing for the approximately 20-25% of the measured hydrogen storage being in the form of electric double layer capacitance that would not be retained after liquid electrolyte removal, the overall retention of hydrogen was 75-80%, a promising initial result.

B. Molecular modelling has shown C…H bonds when hydronium reacts with negatively-charged carbon surfaces

Molecular modelling using Density Functional Theory and Ab initio molecular dynamics conducted as part of this project has shown that reactions between hydronium (H_3O+) and negatively charged graphene surfaces, both with surface oxygen groups and without, can in both cases lead to formation of hydrogen bonded to the surface, and hence effective storage of hydrogen. This form of reaction is crucial for the C-particles to store hydrogen electrochemically as required in this proton reactor system.

C. Cyclic voltammograms of activated carbon from phenolic resin in acid electrolye have shown clear signs of C…H bonding

Cyclic voltammograms taken of activated carbon from phenolic resin in a 1 M dilute sulphuric acid electrolyte have indicated a relatively-strong, but reversible, C..H reaction (or a number of such reactions) in the potential range +0.25 V to -0.25 V (vs Standard Hydrogen Electrode). This provides some experimental evidence that the form of reaction needed in the proposed hydrogenated C-particle storage system is taking place.

Overall the work on the project has been divided into five research streams:

1. Selection of C-particles and electrolyte
2. Design of slurry electrode
3. Design of experimental proton flow reactors
4. Design of separator
5. Computer simulation modelling of the system.

In research stream 1, the candidate carbon-based materials we have focussed on so far as being likely to have such properties are:

- activated carbons, in particular, activated carbon made from phenolic resin, and Norit, a porous carbon made from charcoal or peat
- layered graphitic carbon nitride materials
- layered graphene materials
- single-walled carbon nanotubes.

The best electrochemical hydrogen storage we have found to date has been from activated carbon from phenolic resin, at 0.81 wt%H. We have identified measures to increase this gravimetric energy density significantly. The elemental composition of this sample analysed by X-ray Photoemission

Spectroscopy was 95.9% C and 4.1% O, with around 61% of this carbon being sp^2 hybridised (that is, graphitic).

We are planning further experiments to confirm the contributions to H storage in aC from PR of bonding via O functional groups and direct C-H bonding. These results should then guide us in modifying the composition of this material during synthesis in order to achieve a significantly higher H storage capacity, with less reliance on double layer capacitance.

In research stream 2, fundamental work on slurry electrode design has focussed on ANSYS simulation modelling of a slurry of carbon particles in water to improve understanding of how the key factors – such as concentration, particle size and flow rate – affect the electron conductivity of the slurry. In addition, progress has been made in designing both a microfluidic test system, and a larger scale system with a carbon foam current collector, for measuring the performance of a slurry electrode, and an overall proton flow reactor.

Within research stream 3, a proton reactor with a paste electrode has been designed, constructed and operated, to show the technical feasibility of the overall proton flow reactor, as described above. Linked with research stream 4, this system has tried out two methods of separating the liquid from solid in a paste electrode: vacuum drying and argon drying. The latter has so far proved most effective.

In research stream 5, a simulation model for the whole proton flow reactor system for electrical energy storage on grids, and export of hydrogen made from renewable energy in Australia in the form of hydrogenated C particles, has been constructed in Matlab software. The model includes mathematical representations of all the main components. It is intended primarily to calculate the overall energy efficiency of the system from experimental performance data on components obtained in this project; and estimate the range of levelised cost of delivered electricity after bulk storage in Australia, and after export internationally, obtainable from a scaled-up system of this kind.

On the basis of the achievements to date in this project, RMIT University has submitted an application for a patent for the overall proton flow reactor system. Once this patent is accepted, we plan to publish a number of papers on the scientific advances made so far, in journals such as *Nature Energy*, *International Journal of Hydrogen Energy*, and *Carbon*.

It is important to note that experimental work on this project has effectively been stopped since early March this year when RMIT University laboratories were closed due to Covid-19 restrictions. However, from the experiments done up to that time, and the associated theoretical and computer simulation analysis, we have still been able to achieve Milestone 2 in this project by the due date.

In summary, highlights in the project to date are:

- Experimental demonstration of a proton flow reactor system with a paste electrode made from activated carbon from phenolic resin
- Quantum-theory based molecular modelling and experimental cyclic voltammetry that have shown reactions between hydronium (H_3O+) and negatively-charged carbon surfaces leading to bonding of hydrogen to the surface.

Key difficulties encountered have been:

- Pinpointing the exact form of the electrochemical reactions taking place between hydrogen and carbon surfaces within activated carbon from phenolic resin
- The halt to all experimental work on the project due to Covid-19 restrictions since March this year.

4 Commentary on commercialisation prospects

The key achievement relating to commercialisation of this proton flow reactor system has been the lodging of an application to IP Australia for a provisional patent for this technology.

It is planned in the next part of the project to estimate the potential overall roundtrip energy efficiency of this system for storing electrical energy and exporting a hydrogen-based fuel produced from renewable energy in Australia for use in generating electricity overseas. In addition, estimates will be made of the corresponding prospective levelised costs of delivered electricity. These projections will enable a realistic assessment of the competitiveness of this technology vis a vis other zero-emission alternatives – such as ammonia and liquid hydrogen made entirely from renewables – to be made. This will open up discussions on commercialisation prospects.

5 Knowledge-sharing activities completed

We have restricted presentations on this technology and the project itself at scientific, technical and industry-based conferences and workshops, until protection of the intellectual property involved has been applied for. Now that a patent application has been lodged, we plan for a number of papers on the scientific advances to be submitted to journals, and attendance of project research personnel at relevant conferences and workshops will be encouraged.

There have nevertheless been a number of knowledge-sharing activities conducted since the project commenced, focussing on general aspects of the project and the technology as detailed in Table 1.

Table 1: knowledge-sharing activities conducted since the project commenced

Researcher	Date	Knowledge sharing activity	Event/organisation	Location
Professor John Andrews	6-9 November 2018	Technical visit and presentation (8 November 2018)	International Institute for Carbon Neutral Energy Research (I2CNER) and Kyushu University	Fukuoka, Japan
		Presentation video	Made available via YouTube by I2CNER	www.youtube.com/watch?v=UIXzhE7KS18
	12 November 2018	Technical visit and discussions	Eldor Corporation (industry partner) Research Laboratory.	Orsenigo, Italy
	16 November 2018	Presentation to President and senior management, and discussions	Eldor Corporation (industry partner), President's residence,	Castiglione d'Orcia, Italy
	20 November 2018	Technical visit	Precors (fuel cell bipolar plate manufacturer)	Julich, Germany
	22 November 2018	Technical visit and presentation	Department of Chemistry, University of Cambridge	Cambridge, UK
RMIT ARENA project research team	20 November 2019	Technical workshop	I2CNER and Kyushu University, Japan, visit by Professors H. Matsumoto and T.Fujigaya and PhD student	RMIT Melbourne
RMIT ARENA research team	27 November 2019	Video presentation on progress	Eldor Corporation	Melbourne/Italy
Professor Gary Rosengarten	20 June 2019	Technical visit and discussions	Prof. Jean-Luc Meunier, Plasma Processing Laboratory, Dept of Chemical Engineering, McGill University leading to sending sample carbon nanotubes being sent for testing stability, conductivity and H- storage potential	Montreal, Canada
Dr Seyed Niya	4 December 2019	Conference presentation	Australian Nano and Energy Materials 2019 Conference	University of Western Australia, Perth
Prof. John Andrews and Prof. Gary Rosengarten	2019-2020	Project description	RMIT website	https://www.rmit.edu.au/research/our-research/enabling-capability-platforms/information-systems-engineering/energy/research-areas/conversion-and-storage
RMIT/Prof. John Andrews, Prof. Gary Rosengarten, Dr Shahin Heidari, Sr Seyed Niya, Saeed Seif Mohammadi, Francois du Toit	June 2020	Provisional patent application lodged with IP Australia	"Proton Flow Reactor System"	Melbourne