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Electrochemical generation of ozone with up to 50% current efficiency in 0.5 M sulphuric acid at room temperature and cell voltages < 3 V

Newcastle University

Outline of this Talk

- Objectives
- Introduction
- Experimental
- Results and discussion
- Conclusions
- Acknowledgements

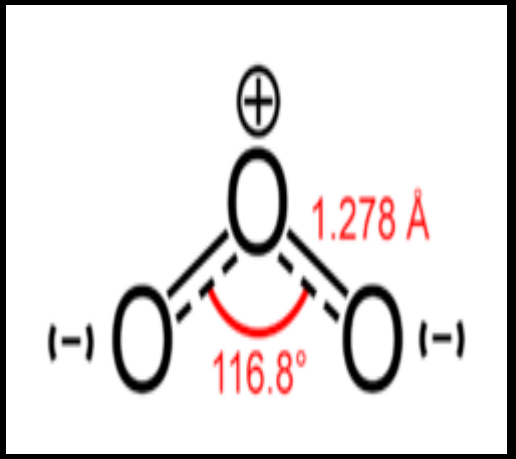
Objectives

- To develop an efficient, cost effective, electrochemical ozone generator

- To compare the performance of the electrochemical system to cold corona discharge (CCD) ozone generation

Ozone

- Strong oxidizing agent
- Clean chemical agent



Application in

* Sterilization
* Deodorization
* Decolourization
* Water treatment

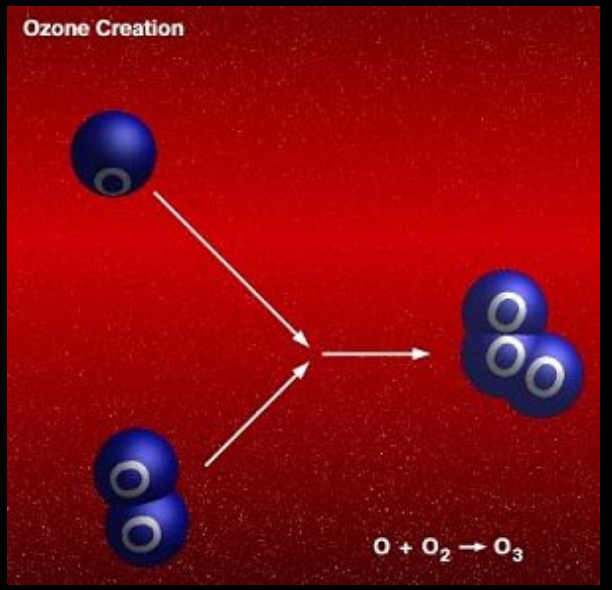
Ozone Generation

- Photochemical
- Cold Corona Discharge (CCD)
- Electrochemical

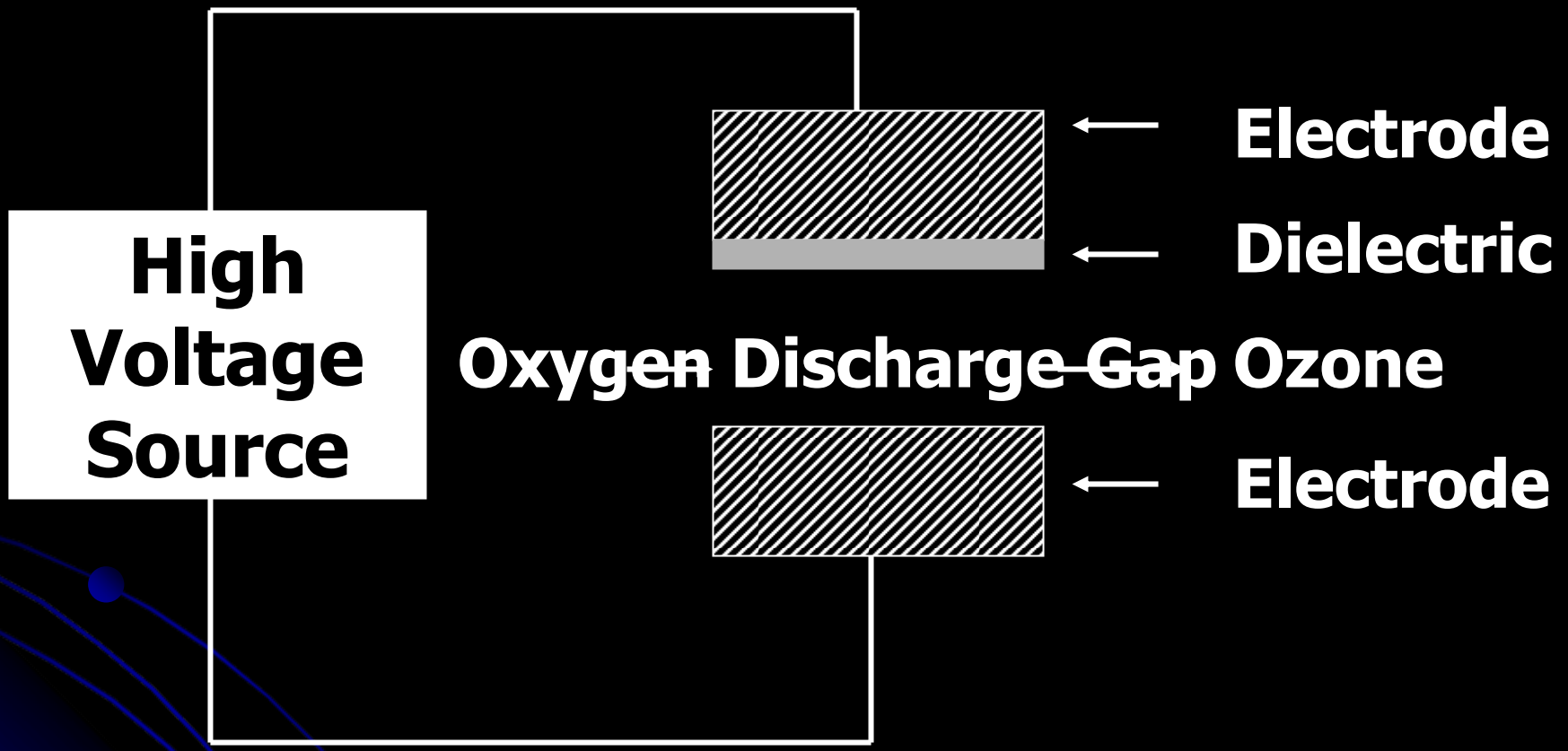
Photochemical

$O_2 + h\nu \rightarrow 2O\cdot$

$O\cdot + O_2 \rightarrow O_3$



Cold Corona Discharge (CCD)

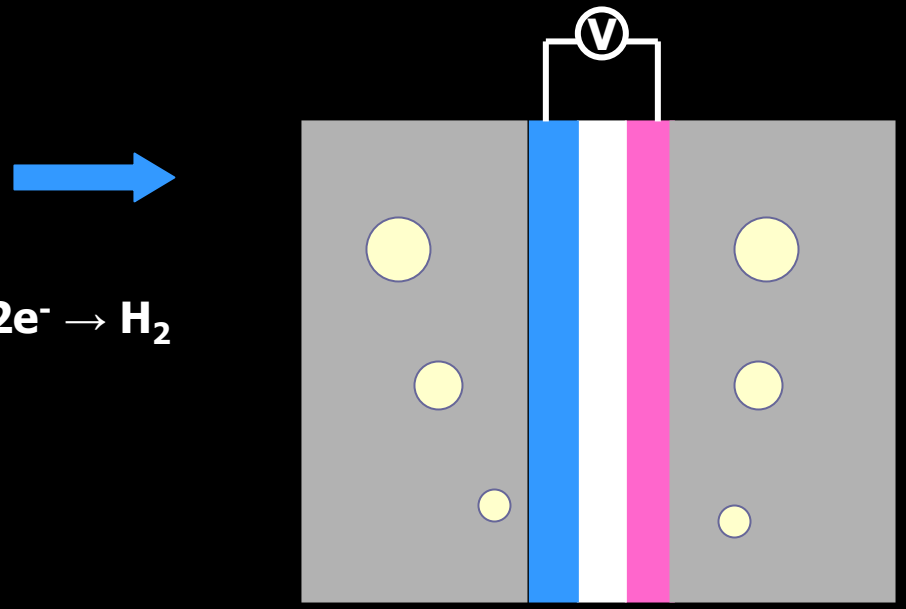


A Schematic diagram of the corona discharge generator

Disadvantages of Cold Corona Discharge (CCD)

- Low concentration of O_3 , 12% by volume
- Generate only gas phase O_3
- Requires high voltage (kV range) power supplies
- Requires cold, dry and pure O_2
- If air is used nitrous oxides are produced and O_3 efficiency lowered
- Implementations are not physically robust

Electrochemical Generation



$2H^+ + 2e^- \rightarrow H_2$

$O_3 + O_2$

$3H_2O \rightarrow O_3 + 6e^- + 6H^+$

$2H_2O \rightarrow O_2 + 4e^- + 4H^+$

Acid Electrolyte

Mesh Anode Coated with doped SnO_2

Nafion Polymer Electrolyte

Pt/Ti mesh Cathode

Acid Electrolyte

Advantages of electrochemical approach

- Very high concentrations possible in the gas and liquid phases
- Simple system design
- No need for gas feeds of any description
- Robust
- Low voltage operation

Evolution of electrochemical ozone generation

Foller and Tobias :

- **Under acidic conditions at 0 to – 64 ^{0}C with current efficiencies 20-35%**
- **Employing F^-- containing electrolyte**
- **50% using a carbon anode in 7.3 M HPF_6 at 0 ^{0}C**

K Y Chan :

- **Adding Ni to Sb-doped SnO_2 anode in 0.5 M H_2SO_4 at low applied potentials (cell voltage < 3V) and with current efficiencies of *ca*. 35%**

Experimental

- Anode preparation
- Ozone measurement
- Electrochemical cell and systems
- Calculation of current efficiency

Anode preparation

The anodes were prepared following the procedure of Wang et al. using 6.3 cm^2 Ti mesh substrates with Sn:Sb:Ni molar ratios (in the precursors) of 500:8:2, 500:8:3 and 500:8:4 (0.02 to 0.4 wt% Ni). Wang et al. typically applied 7 dip coats, judging this to be thick enough to completely cover the underlying Ti mesh. However, we applied 20 coats, based on the work of Montilla et al. who found that the EDX signal from the underlying Ti mesh decreased below the level of detection only after 20 coats were applied. Pt/Ti mesh (5 cm x 5 cm) was employed as the counter electrode.

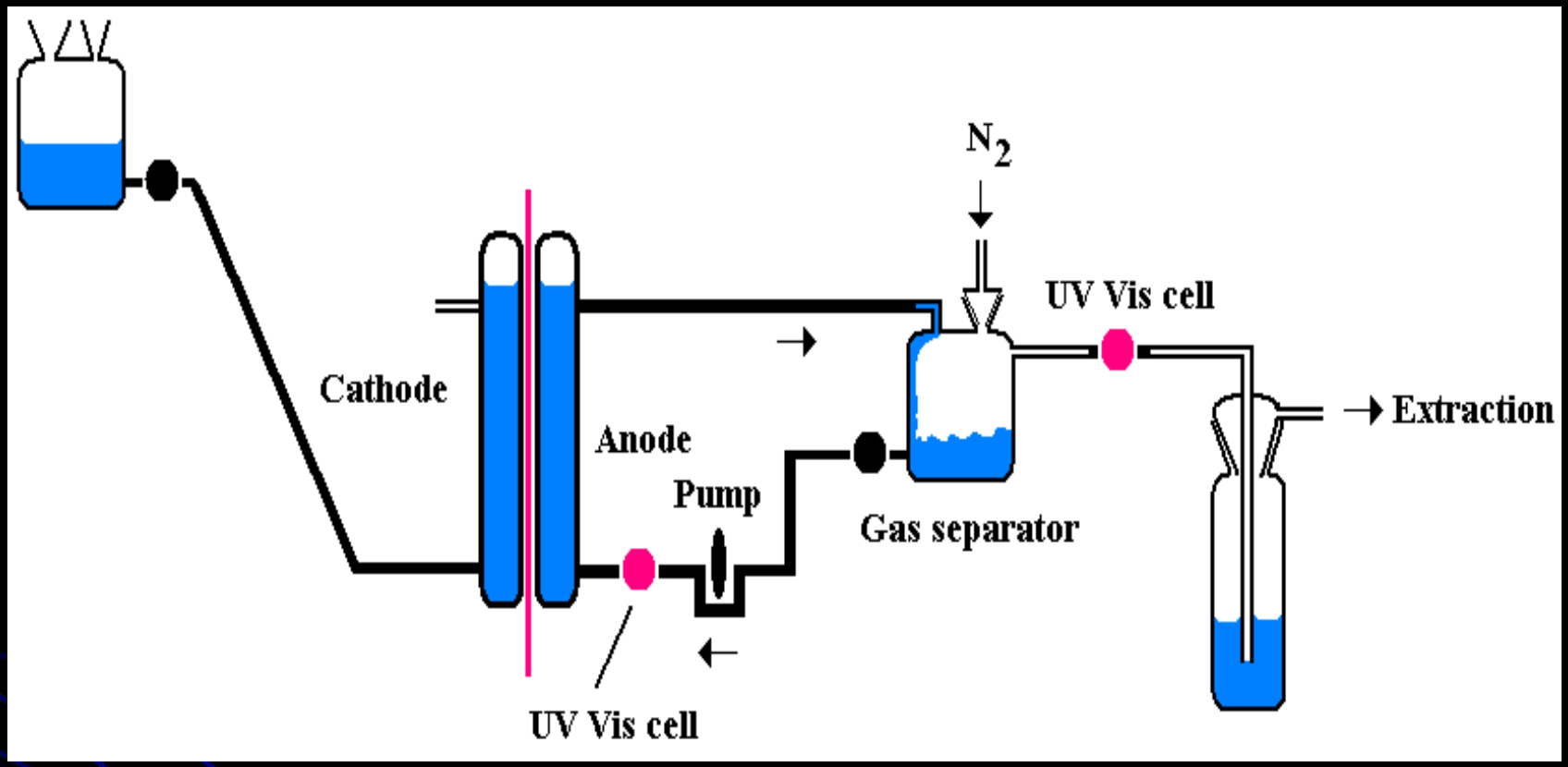
Ozone measurement

- **Astranet UV-Vis fibre optic spectrometer system**
- **The value of the extinction coefficient for gas and liquid phase ozone at ca. 258 nm was 3000 mol^{-1} dm^3 cm^{-1}, as recommended by International Ozone Association**

Electrochemical cell and systems

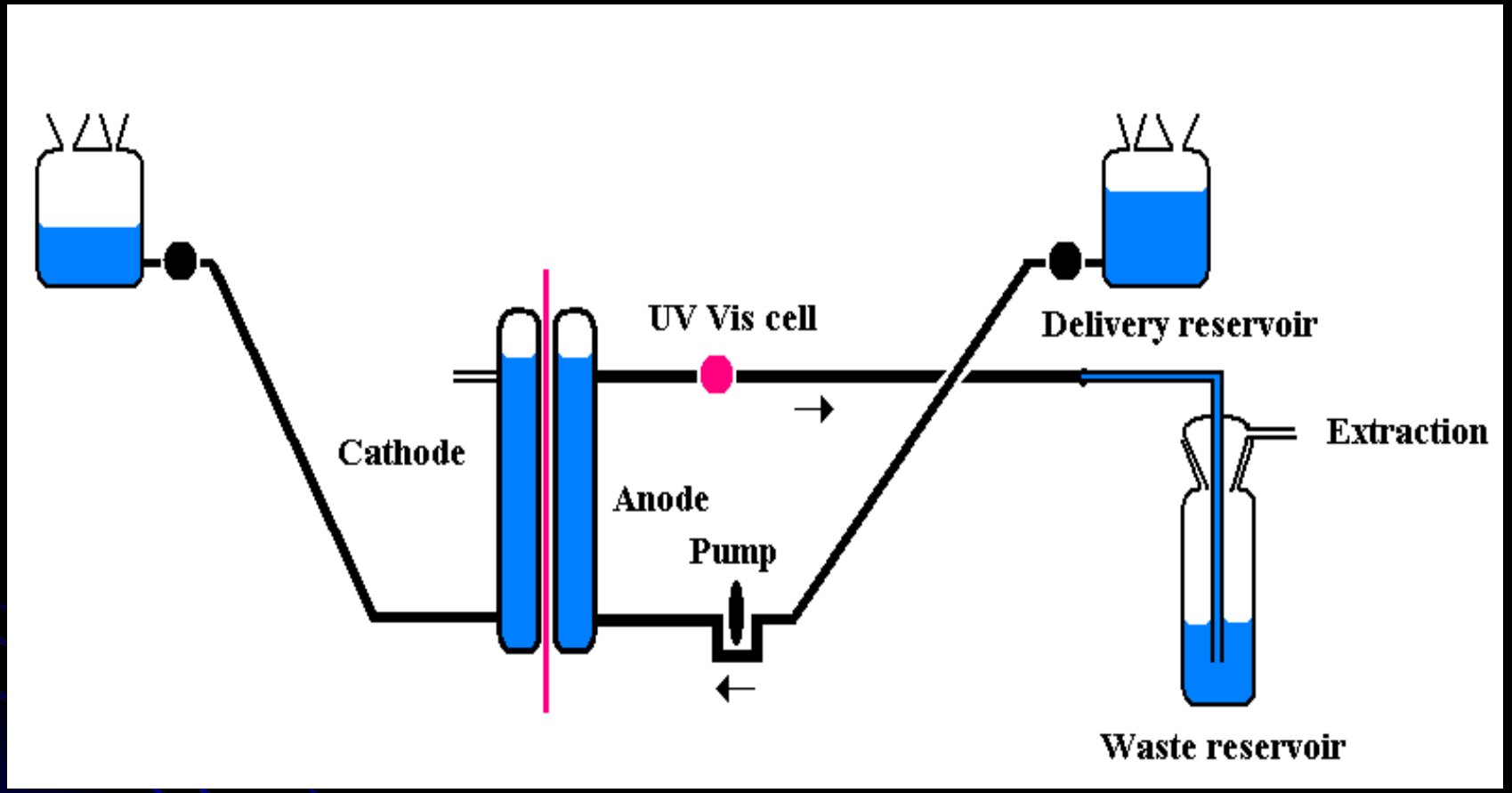
The electrochemical cell

Electrochemical cell and systems



Schematic representation of the electrochemical cell and system employed in the anolyte recycle experiments, N_2 gas was used to dilute the anode gas steam

Electrochemical cell and systems



Schematic representation of the electrochemical cell and system employed in the anolyte flow experiments

Calculation of current efficiency

Absorbance A = $\varepsilon c l$

$$\eta = n_{O3}/n'_{O3} = 6FA\,f/\varepsilon I600 = 0.32A\,f/I \quad (1)$$

Calculation of energy consumption

$$N = 6\,\eta\,I\,F$$

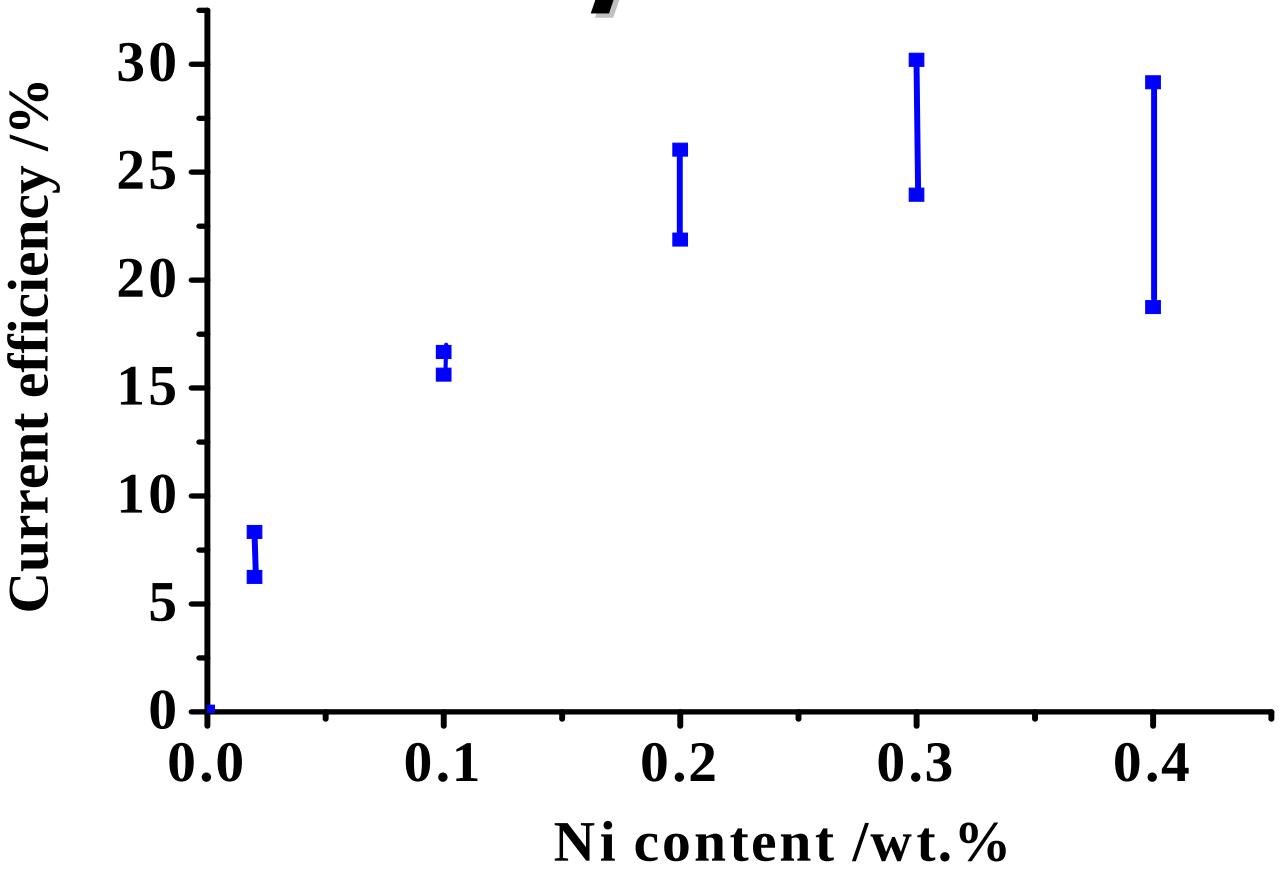
$$Po_3 = 335\,V/\eta \text{ kWh kg}^{-1}\ O_3 \quad (2)$$

η = T efficiency in %, ε = The extinction coefficient (3000 $mol^{-1}\ dm^3\ cm^{-1}$), *f* = Flow rate (ml min^{-1}), c = Concentration of ozone (mol dm^{-3}), *l* = The path length (1 cm), F = The Faraday constant, n_{O3} = Number of moles of O_3 produced, n'_{O3} = Number of moles of O_3 assuming 100% efficiency

Results and Discussion

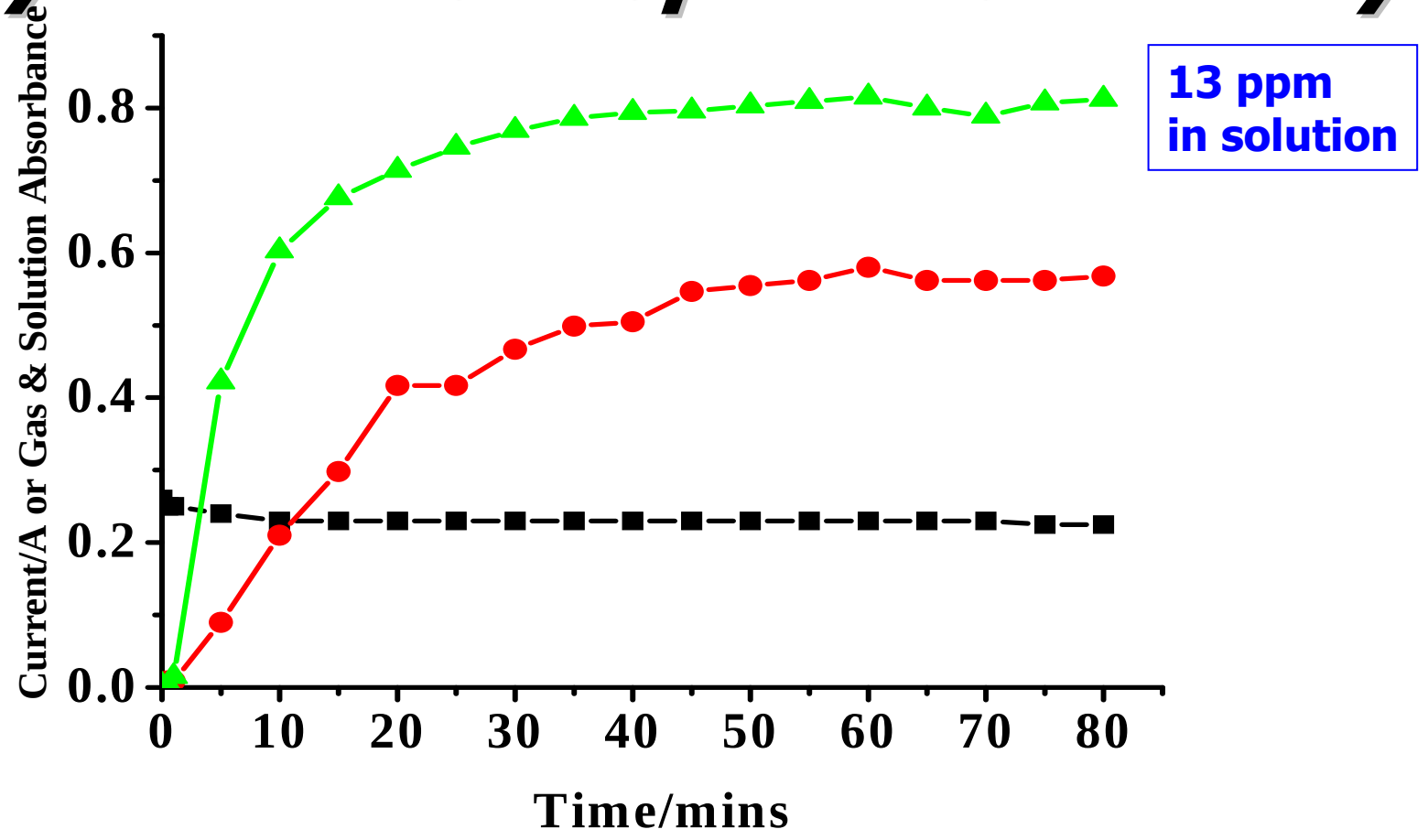
- Optimum Ni content
- Recycle *vs* flow operation
- Synthesis reproducibility and maximum current efficiency
- Operational and cost comparison with CCD

The optimum Ni content



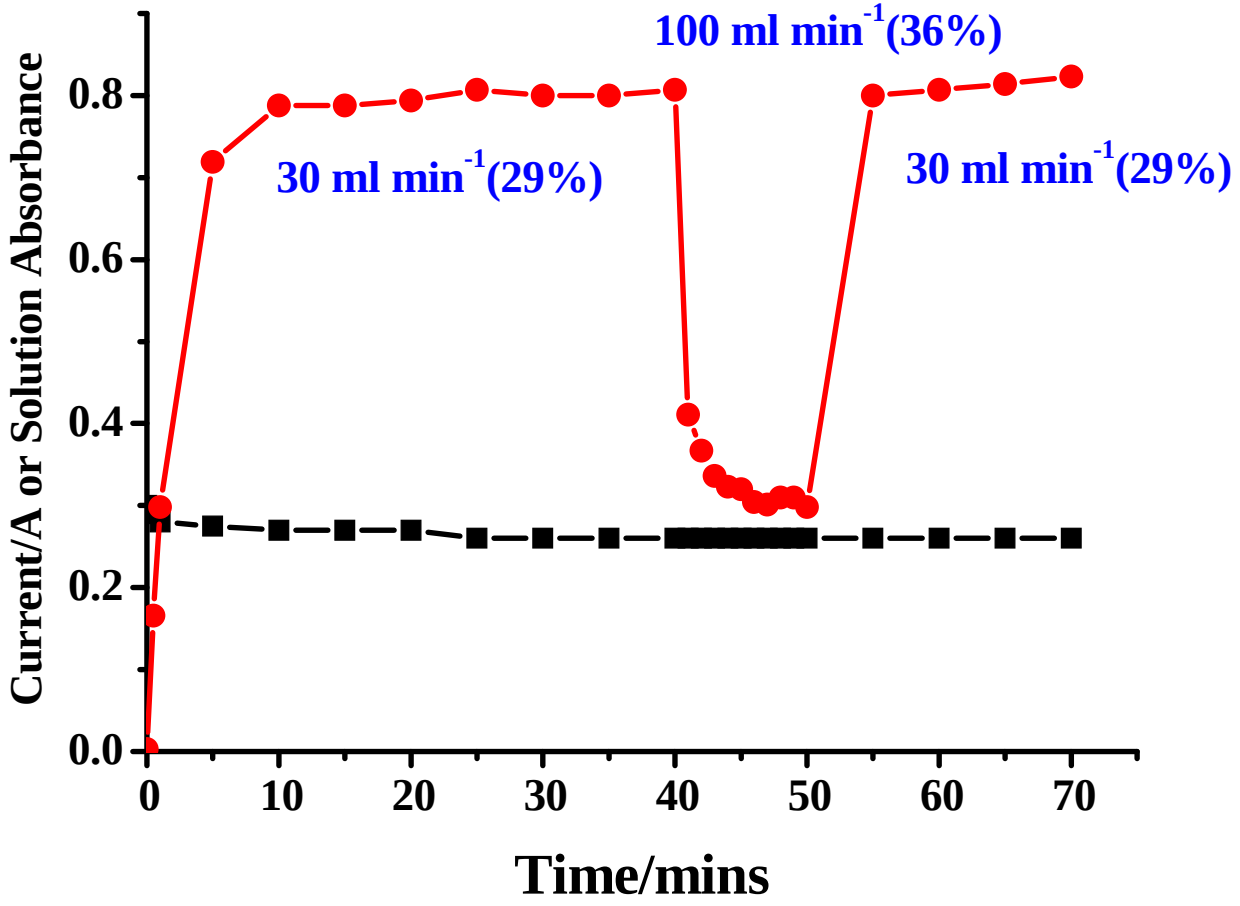
Plot of the minimum current efficiency measured by the flow approach at a cell voltage of 2.7 V and anolyte (0.5M H_2SO_4) flow rate of 30 ml min^{-1} as a function of the Ni content of the anode catalyst, eg. 0.3 wt% = 500:8:3 Sn:Sb:Ni in the precursor mixture. The anodes were 2.5 cm x 2.5 cm meshes and the points at each Ni content are efficiencies measured in two runs

Recycle vs flow operation-always



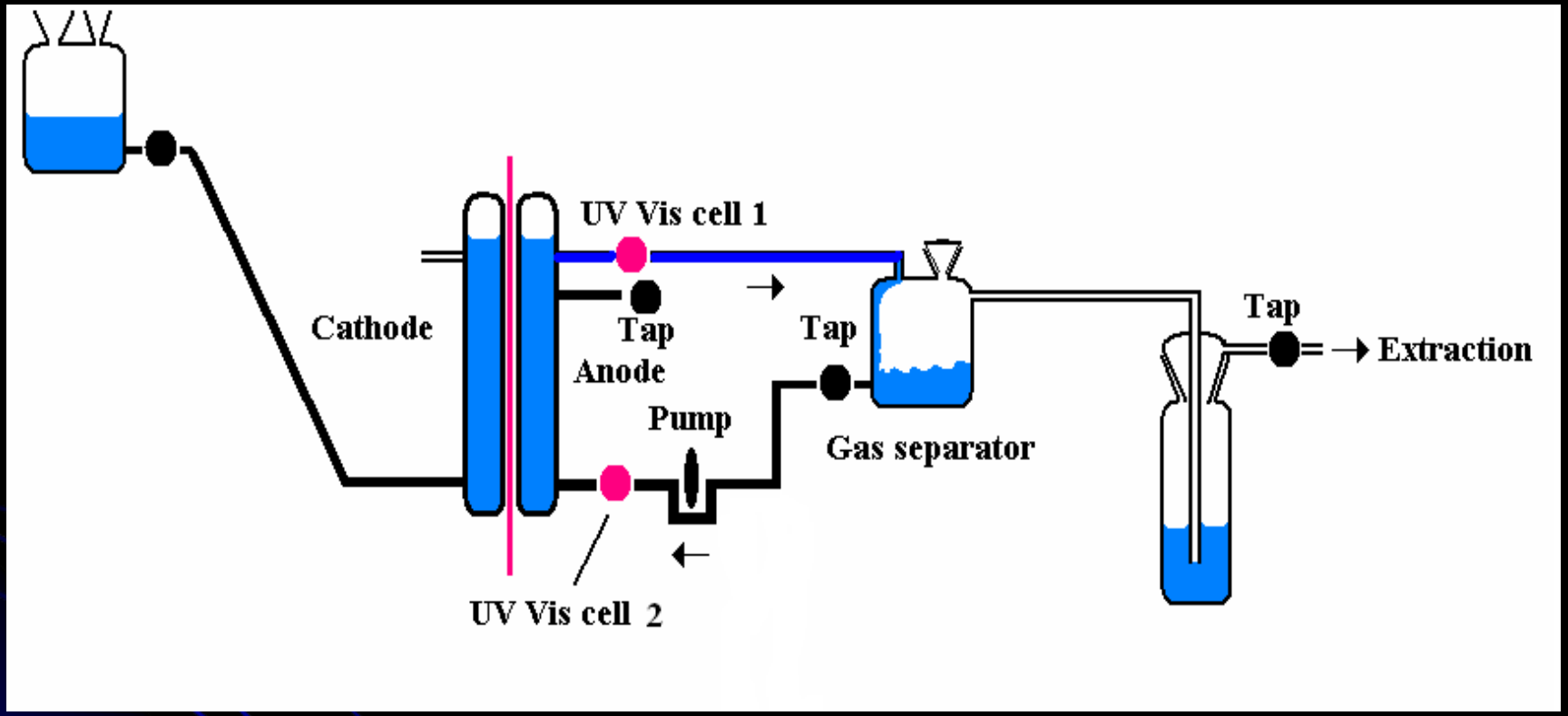
Plots of current (■), gas-phase ozone absorbance (●) and solution ozone absorbance (▲) during a recycling experiment using a 2.5 cm x 2.5 cm 500:8:3 Sn:Sb:Ni anode at a cell voltage of 2.7V and an anolyte flow rate of 30 ml min^{-1}, N_2 flow rate was 10 ml min^{-1}

Recycle vs flow operation-typic



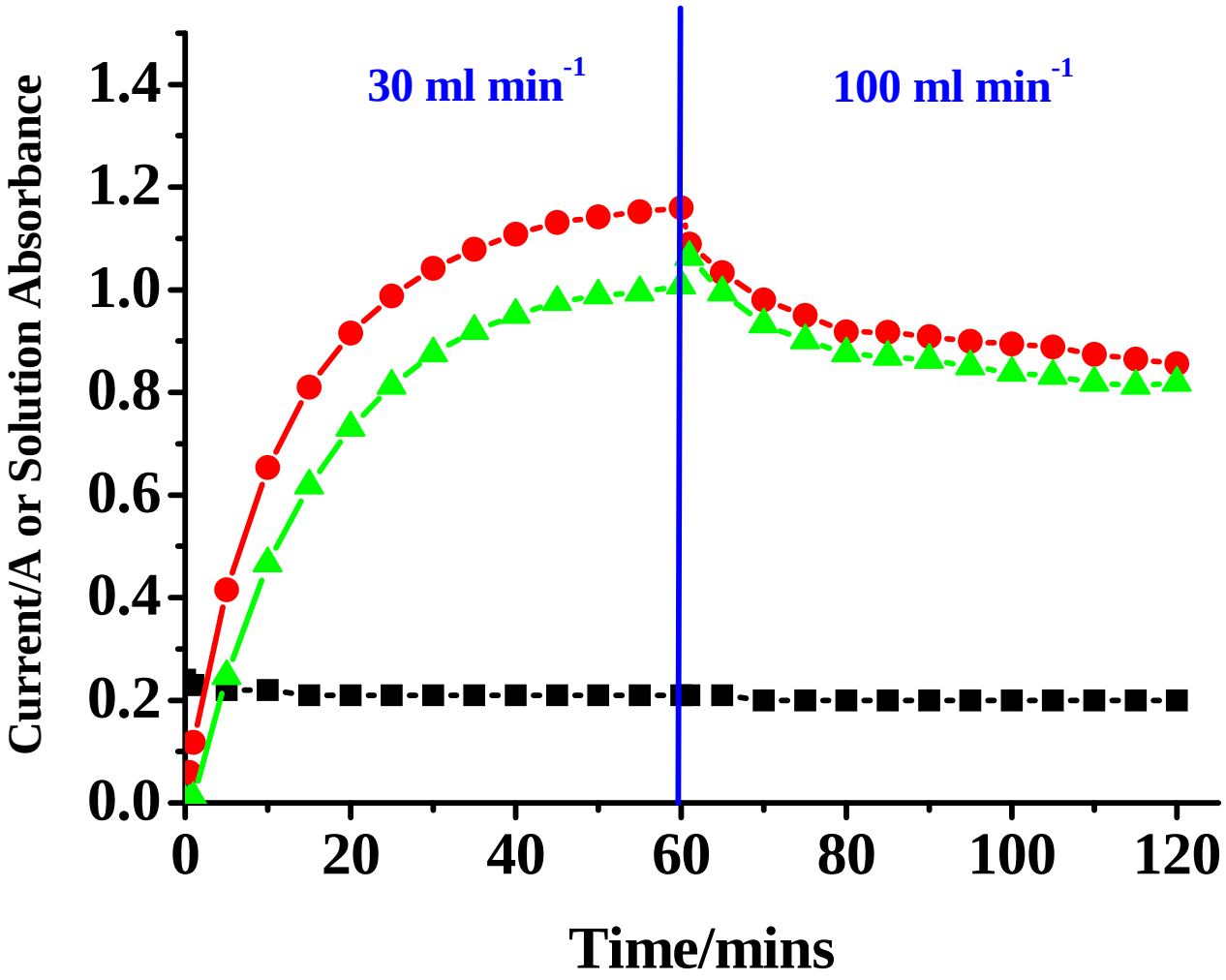
Plots of the solution O_3 absorbance (●) at the outlet of the electrochemical cell and current (■) vs time at a cell voltage of 2.7 V and anolyte flow rate of 30, 100 and 30 ml min^{-1} using the anode in above

Recycle vs flow operation



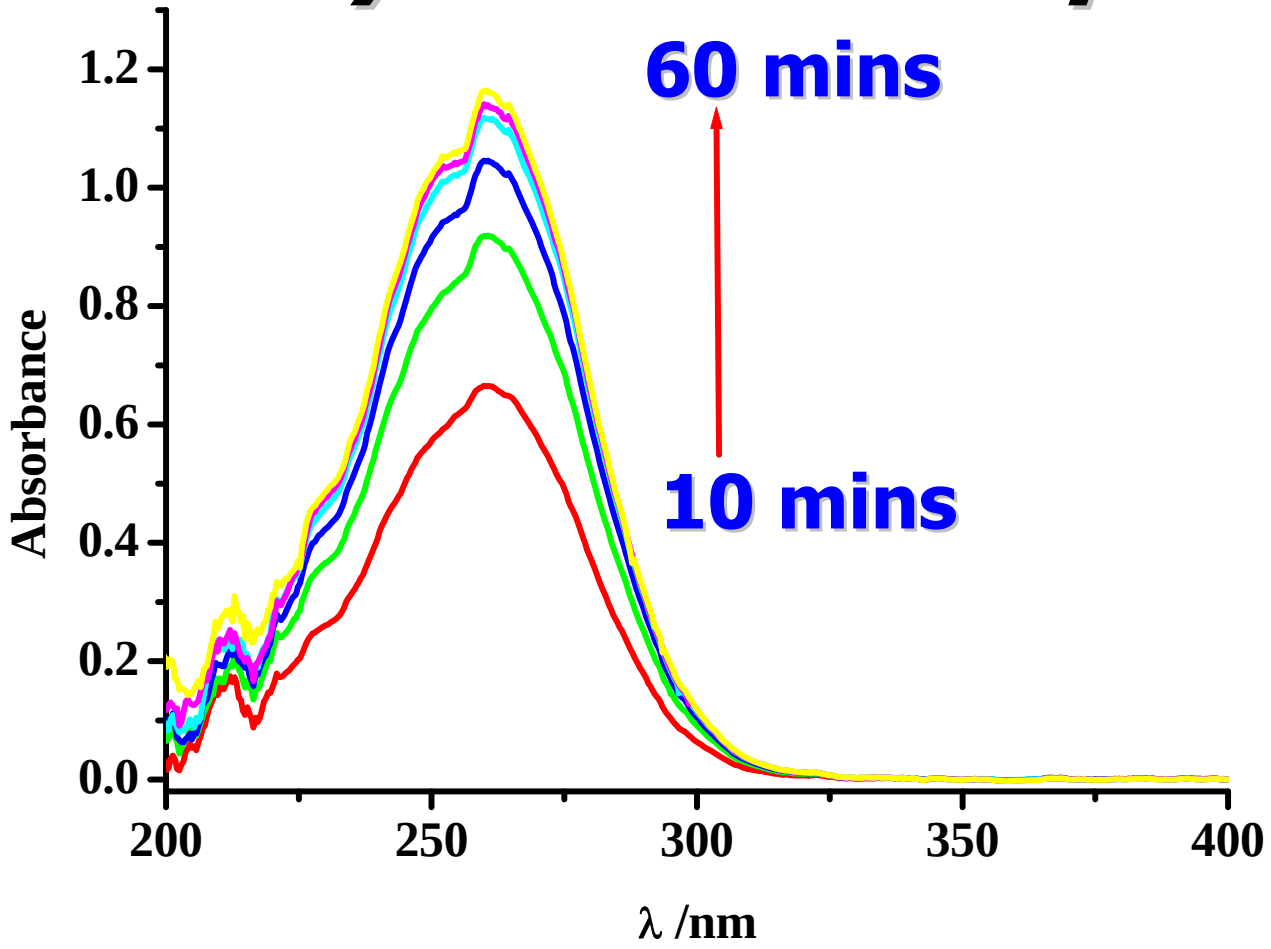
Schematic representation of the electrochemical cell and system in the modified recycle experiments

Recycle vs flow operati



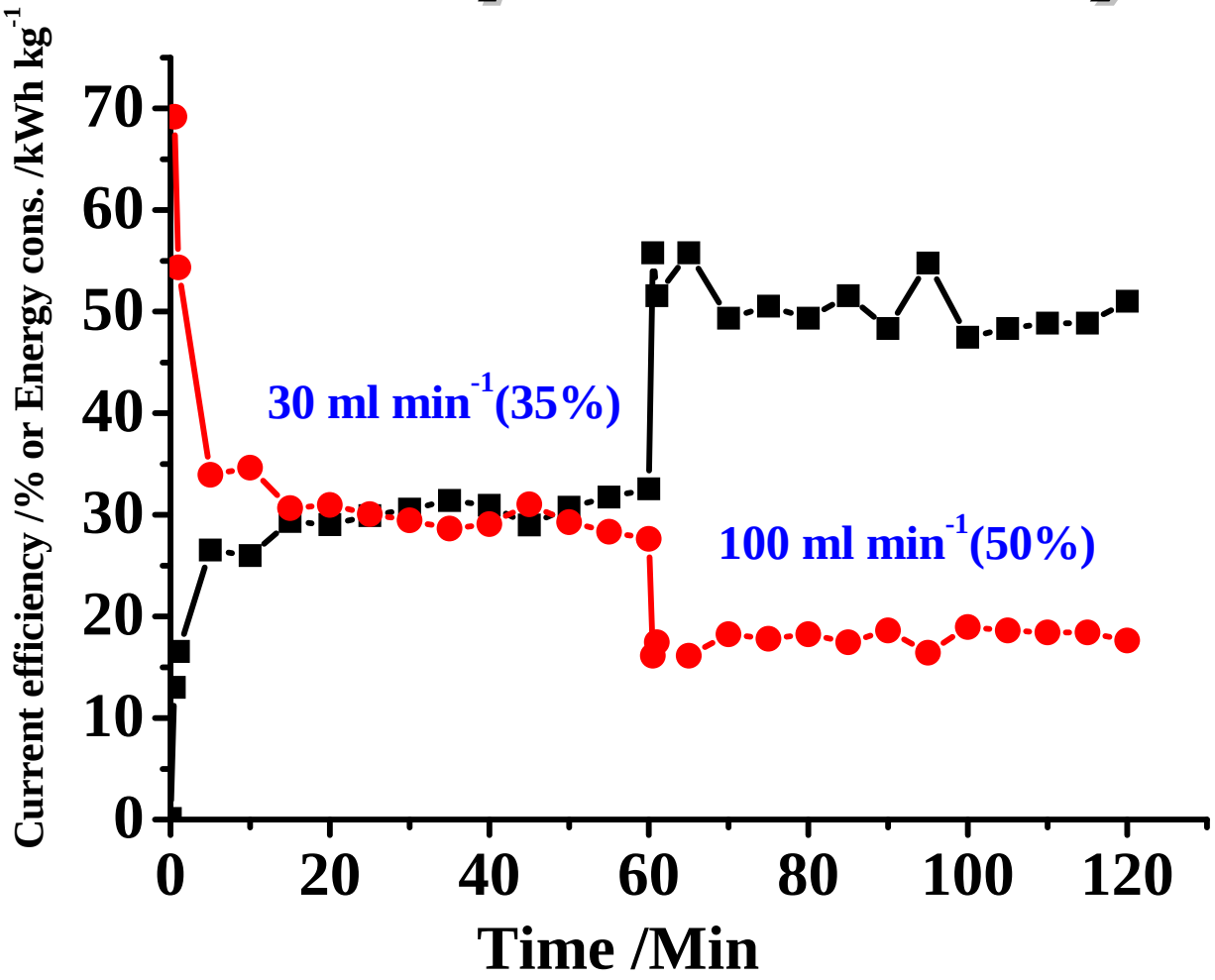
Plots of the current (■) and inlet (▲) & O_3 outlet (●) absorbances as a function of time during a recycling experiment using the same anode at a cell voltage of 2.7V and flow rates of 30 & 100 ml min^{-1}

Recycle vs flow operation –



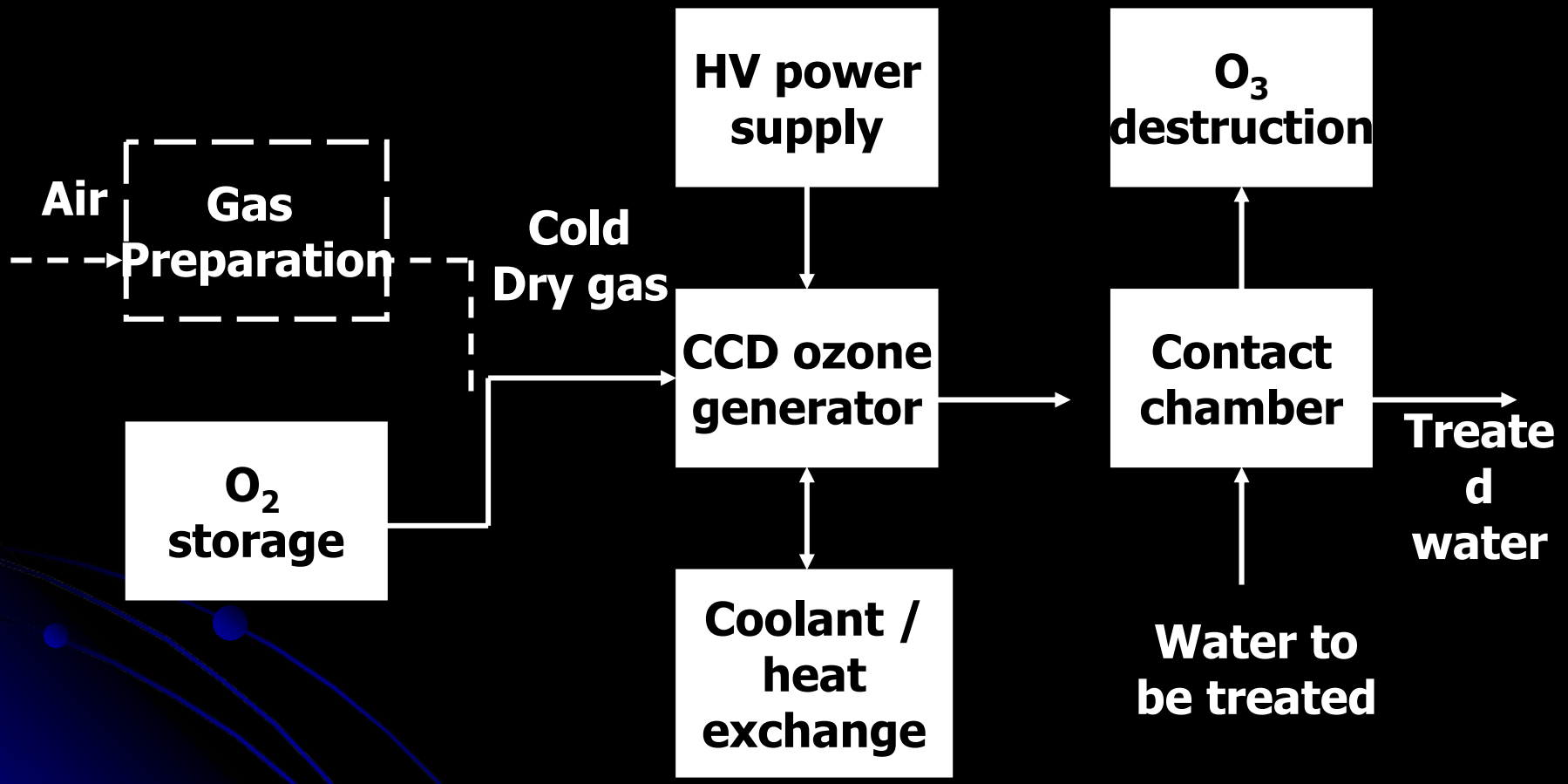
UV-Vis spectra taken at the outlet of the electrochemical cell during the experiment above; the first spectrum was collected after 10 minutes electrolysis, and the remaining spectra at 10 minute intervals thereafter. The peak absorbance increases with electrolysis time

Synthesis reproducibility and ma



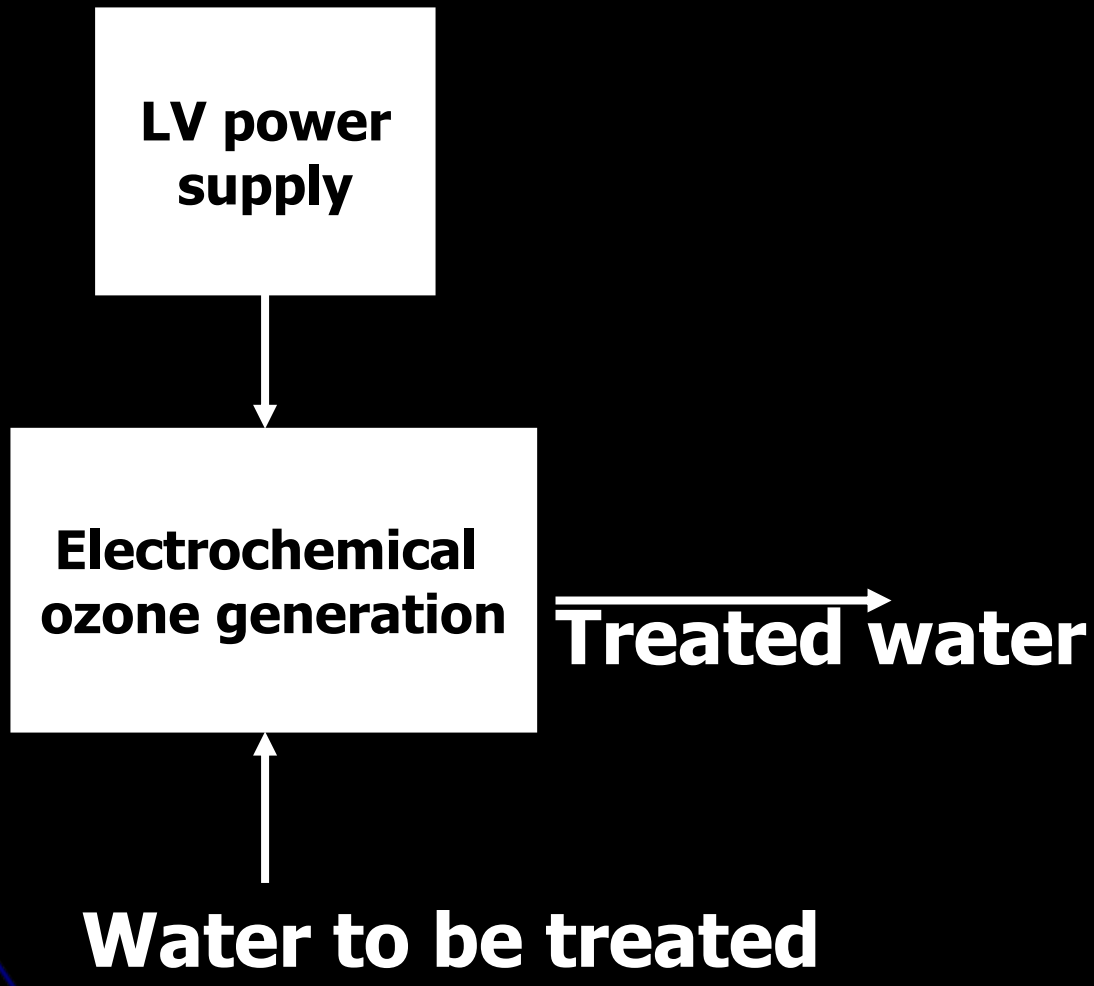
Plots of current efficiency (■) and specific energy consumption (●) vs time during a flow experiment at a cell voltage of 2.7 V using a 2.5 cm x 2.5 cm 500:8:2 Sn:Sb:Ni anode

Operational and cost comparison with CCD



Schematic of a Cold Corona Discharge ozone generation system

Operational and cost comparison with CCD



Schematic of an electrochemical ozone generation system

Energy consumption estimates for ozone generation systems

(kWh / kg)	Values for Ni-doped electrochemistry		Our estimates for CCD		Tchobanoglous et al. for CCD	
	Min	Max	Min	Max	Min	Max
Gas preparation / handling	0	0	2.4	3.3	4.4	6.6
O_3 generation	18.0	24.2	8.0	16.0	6.6	19.8
Cooling	0	0	2.4	4.8	0	0
Ozone contacting	0	0	2.2	6.6	2.2	6.6
All other uses	0.3	0.6	1.2	2.2	1.2	2.2
Total excluding O_2	18.3	24.8	16.2	32.9	14.4	35.2
Liquid O_2 production	0	0	1.7	5.0	1.7	5.0
Total including O_2	18.3	24.8	17.9	37.9	16.1	40.2

Conclusions

- Giving highly active and selective Ni/Sb-SnO_2 anodes
- Giving current efficiencies up to 50% for ozone generation under flow conditions at room temperature and a cell voltage of 2.7 V
- Giving the optimum selectivity of mole ratios between 500:8:2 and 500:8:4 Sn:Sb:Ni in the precursor solution
- Giving an electrical energy consumption of 18 kWh kg^{-1}

Acknowledgements

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Thank You