



Improved Durability and Cost-effective Components for New Generation Solid Polymer Electrolyte Direct Methanol Fuel Cells

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DELIVERABLE REPORT

D.2.2 – PROTOCOLS FOR EX-SITU CHARACTERISATION OF CATALYSTS		
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NATURE OF THE DELIVERABLE		
R	Report	X
P	Prototype	
D	Demonstrator	
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SUMMARY	
Keywords	<i>Catalysts, Characterisation, Protocols</i>
Abstract	<p>The objective of this deliverable is to define characterisation and test protocols for the assessment of relevant properties including catalytic activity and durability characteristics of the newly developed DMFC electrocatalysts. The procedures used as means of verification to assess the achievement of project milestones are identified.</p>

REVISIONS			
Version	Date	Changed by	Comments
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D.2.2 – PROTOCOLS FOR EX-SITU CHARACTERISATION OF CATALYSTS

I. INTRODUCTION

This deliverable concerns with:

-Individuation of a set of characterisation and testing protocols for an ex situ characterisation of DMFC electro-catalysts including steady-state and accelerated durability tests as well as performance evaluation in relation to the specific applications.

-Establish a benchmark of baseline components against which progress may be assessed in terms of durability, performance and cost.

Electro-catalysts testing protocols, parameters and procedures are defined to allow for a homogeneous screening and evaluation of the newly developed components. Appropriate testing protocols are necessary to screen the best performing anode and cathode catalysts prepared with different methods. Measurements protocols are defined for both ex-situ physico-chemical and electrochemical characterizations. The testing procedures are planned to validate the quantitative project targets in terms of performance and durability.

For the electro-catalyst testing, the specifications concern with catalyst loading, catalyst requisites and amounts for provision to WP5 for MEA development.

The identification of the most appropriate physicochemical characterisation techniques and methodologies is necessary for the determination of structure, surface, morphology and chemical properties. These specifically concern with methodologies for the determination of crystallographic structure, particle size and catalyst dispersion, determination of the oxidation state, surface chemistry and segregation characteristics. The aim is to correlate the physico-chemical characteristics to electrochemical properties.

Electrochemical screening of the catalysts ex-situ includes mainly half-cell electrochemical tests. The definition of measurement protocols concerns with cyclic voltammetry, half-cell polarisation curves, rotating disc electrode experiments and ac-impedance spectroscopy measurements.

These protocols are used to investigate the electro-catalyst characteristics as a basis for screening the most promising formulations. Depending on the electrocatalyst properties, it will be identified, time by time, among the overall set of protocols which will be the most appropriate for the specific electrocatalyst characterization to get sufficient insights for the down-selection of the best formulations.

The procedures used as means of verification to assess the achievement of project milestones are identified.

II. PROTOCOLS

1. Catalyst's support assessment:

1.1 Electrochemical tests

These experiments serve as a screening to compare the electrochemical degradation in an acidic environment of different supports. For this experiment, the selected electrolyte is sulphuric acid 0.5 M and the temperature is 75 °C.

The liquid electrolyte provides a proper environment in terms of water content and proton activity; these experiments are useful to predict the level of corrosion in the direct methanol solid polymer electrolyte.

The corrosion of benchmark carbon black supports is the main driving force of cathode catalyst degradation. It is thus appropriate to quantify the corrosion in terms of loss or oxidation of supports during specific electrochemical experiments (accelerated stress tests) at high operating voltages.

It may be also useful to carry out such experiments on both support alone and catalysed support to understand if there is any promoting effect to the support corrosion associated to the presence of a noble metal phase or any other active species. To discriminate between support corrosion and active noble metal phase corrosion, an accelerated procedure consisting in applying 1.4 V RHE for 2 h is selected. This condition allows to discriminate between catalyst and support degradation. Noble metal catalysts such as Pt-based catalysts are covered by an oxide layer that protects the metal phase from corrosion at these potentials. Support degradation is estimated in terms of loss/oxidation of support from the integrated corrosion current.

Ex-situ physico-chemical analyses, pre and post operation, are carried out by XRD, XPS, TEM, SEM-EDX and XRF. These serve to individuate structural, chemical, surface and morphology changes in the support as a consequence of the accelerated test protocol.

To assess the stability in the entire thermodynamic potential window, cyclic voltammetry experiments are carried out in the range 0-1.2 V RHE at different scan rates (s.r.) including 20, 50, 100 and 150 mV s⁻¹. Modification of the electrochemical double layer characteristics as a function of the cycle numbers and the sweep rate is used to assess the stability in the operating potential window.

AC-impedance spectra are used to assess the series resistance (Rs) of the support in the electrode configuration (loose powders) in a reference electrolyte such as 0.5 H₂SO₄. Rs divided by the support loading is used as parameter to compare the different electronic percolation properties of the novel supports and compared to the benchmark carbon blacks.

The main protocols for supports characterization are summarised in Table 1.

Table. 1

Protocol Category	Properties addressed	Experiment	Parameter to be determined	Screening/ Milestone addressed
Accelerated Stress test	Support degradation	Chrono-amperometry at 1.4 V RHE for 2 h 0.5 M H ₂ SO ₄ at 75 °C	Oxidation charge normalised by support loading	Pre-screening
Accelerated Stress test	Support stability in the operating potential window	Cyclic Voltammetry between 0-1.2 V RHE 0.5 M H ₂ SO ₄ and/or relevant ionomers	Change in the CV profile as a function of cycle number and s.r.	Pre-screening
Electrochemical test	Electronic percolation	AC-impedance spectra in the range 1 MHz-10 mHz (10 mV r.m.s.) 0.5 M H ₂ SO ₄ and/or relevant ionomers	Normalised R _s (Ohm cm ² mg _s ⁻¹). R _s determined as high frequency intercept on the real axis	Pre-screening

1.2. Out-of-cell studies

Assessment of the catalyst physico-chemical properties is carried out by using a set of characterization techniques available within the Consortium. The necessary characterizations to provide a fingerprint of the catalyst properties are identified below:

-Structural characterization of the catalysts is carried out by X-ray diffraction. Estimation of the crystallite size is made from the peak broadening by using the Debye Scherrer equation. As an example, the peak profile of the (220) reflection in the face centered cubic structure of Pt, Pd and Pt-alloys is analysed by using the Marquardt algorithm to determine the peak width.

- Elemental analysis is carried out by X-ray fluorescence (XRF) and CHNS-O analysis is specifically used for the light elements.

- Morphology is studied by TEM and particle size distribution as well as mean particle size determined by the atomic contrast procedure.

- Surface chemistry including concentration of surface elements and oxidation states is studied by X-ray photoelectron spectroscopy (XPS). The Ag 3d_{5/2} peak of an Ag foil is taken, after argon sputtering, for checking the calibration of the binding energy (BE) scale. The quantitative evaluation of each peak is

obtained by dividing the integrated peak area by atomic sensitivity factors, which are calculated from the ionization cross-sections, the mean free electron escape depth and the measured transmission functions of the spectrometer.

-Loading of active catalyst phase (e.g. Pt, Ru, Pd, no-noble active phase) is determined by common analytical tools such as XRF, spectrophotometry, thermo-gravimetric. As an example, in the case of Pt/C catalyst, the Pt concentration on the support is determined by thermo-gravimetric analysis (by burning the carbonaceous support while measuring the weight changes) followed by XRD analysis of the residue.

2. Electro-catalyst evaluation:

2.1 General procedures

Screening of catalysts will be carried out at both half cell and single cell level in the presence of reference electrolytes and polymer membranes developed in the project. The tests in single cell, specifically dealing with catalyst characterization, are carried out in the driven-mode using a proper floating reference electrode. These tests are reported as ex-situ tests, because during the experiment the single cell does not operate in the normal fuel cell mode. Such a method will allow to test the electro-catalyst in the presence of a variety of polymer electrolytes to get information about the specific anodic or cathodic activity/stability and interfacial properties.

The relevant tests are described below:

- Half cell investigation is carried out with regard to both oxygen reduction and methanol oxidation to individuate activation overpotentials, stability in acidic environment and electrocatalytic activity. The reference temperature for half cell testing in liquid electrolytes, such as 0.5 M H₂SO₄ or 0.1 M HClO₄, is 75 °C.

- Electrocatalyst screening in single cell is appropriate to evaluate electrocatalytic activity and degradation characteristics both at low (20°-90°C) and high temperature (from 100 °C to 110-130 °C). This represents a successive step with respect to the testing in liquid electrolyte since such experiments will be carried out when proper ionomers will be available.

The initial reference electrolytes are sulphuric acid (0.5 M, for anode-catalyst testing) or perchloric acid (0.1 M, preferable for cathode-catalyst testing) for operation in liquid electrolyte half cell, Nafion 117 membrane in combination with Nafion ionomer in the electrodes (15-33 wt.% ionomer content in the catalytic layer) for a driven-mode operation single cell. To overcome Nafion 117 dehydration at high temperature and ionomer dry-out, an increase of the operating pressure up to 3 bar abs. as well as the use of thinner Nafion membranes as reference electrolytes will be considered.

The amount of ionomer in the catalytic layer is initially fixed from the previous results. Optimization of this parameter will be addressed in WP5 and specific ionomer contents information will be provided as feed back. The proper amount of ionomer used in successive experiments will result from a proper compromise to achieve appropriate ionic percolation in the catalytic layer while maintaining a suitable electronic

percolation and proper hydrophilic-hydrophobic properties. The aim will be to achieve good triple-phase boundary for the electrochemical process in the catalytic functional layer.

The baseline catalysts will be of E-TEK or Alfa Aesar type widely reported in the literature as standard state of the art components for DMFCs.

2.1 Electrocatalyst screening in half-cell

2.1.1 Cathode Catalyst performance

Cathode catalysts pre-screening is carried out in a liquid electrolyte by half-cell galvanostatic polarization measurements for oxygen reduction in the presence and absence of diluted methanol (0.005 M) simulating the cross-over. These experiments are carried out preferably in pure 0.1 M HClO₄, as the best model-electrolyte for polymer electrolytes and not poisoning the noble metal cathode catalysts, by using gas diffusion electrodes similar to those developed for single cell testing for oxygen reduction. For the oxygen reduction, a sample holder allowing gas supply to the electrode backing layer (GDL side) is used (Fig. 1). The baseline cathodes are consisting of a GDL type and a catalytic layer containing an initial loading of 2 mg cm⁻² Pt or different loadings for novel formulations as well as for Pt-free formulations with an initial ionomer content of 33 wt.%. AC-impedance experiments for cathode operation are carried out at relevant operating potentials (0.7 V RHE). Overpotentials are determined at 0.125 A cm⁻² with the aim to achieving a value lower than 0.4 V IR-free at 20-60 °C as determined from IR-free Tafel plots for the cathode (oxygen feed) in the range 20-60 °C (20 °C step size).

Similar tests are carried out in a driven-mode operating single cell, using hydrogen feed at the anode thus acting as counter and reference electrode. The cathode is fed with oxygen and operates as working electrode. In the driven mode single cell, the operating temperature range should vary from 20° to 130 °C depending on the ionomer electrolyte. Specific amount of diluted methanol is fed into oxygen stream to simulate the effects of a specific cross-over condition (e.g. 0.005 M CH₃OH). Overpotentials are determined at 0.125 A cm⁻² in the low temperature range with the aim to achieving a value lower than 0.4 V IR-free at 20-60 °C as determined from IR-free Tafel plots for the cathode (oxygen feed) in the range 20-60 °C (20 °C step size). Whereas, in the high temperature range overpotentials are determined at 0.5 A cm⁻² at 110-130 °C with the aim to achieving a value lower than 0.4 V IR-free as determined from IR-free Tafel plots for the cathode (oxygen feed).

Reference cyclic voltammetry is carried out in the potential range 0-1.2 V RHE with a sweep rate in the range 20-150 mV s⁻¹. Determination of ECSA for Pt-based cathodes is made by integration of H-adsorption peaks (0.02-0.4 V RHE) after subtraction of double layer charging at 0.4 V RHE. For Pd-based cathodes the PdO reduction peak in the voltammogram is used for an estimation of the ECSA.

For novel formulations, the most appropriate method to determine ECSA will be identified during the course of the project activity.

For detailed mechanistic studies, additional electrochemical testing procedures are carried out to individuate the relevant electrokinetic parameters such as Tafel slope, activation energy, mass activity, specific activity at specific potentials e.g. 0.9 V RHE. These consist in steady-state galvanostatic polarization curves, stability tests (both chronoamperometric and chronopotentiometric) and rotating disc experiments. To get insights into the mechanism, ac-impedance spectra are carried out at relevant operating potentials (0.85 V, 0.7 V, 0.65 V RHE) in the range 1 MHz-10 mHz (10 mV r.m.s.). The series and charge transfer resistance will be determined from the high frequency intercept on the real axis of the Nyquist plot and from the polarization resistances (low frequency intercept of the relevant semicircle).

2.1.2 Cathode Catalyst degradation

The investigation of catalyst degradation in half-cell is carried out by using potentiodynamic cycling at 80°C in 0.5 M H₂SO₄ (sweep rate 20-150 mV s⁻¹). The potential limits are individuated in 0.6 V - 0.9 V RHE to explore catalyst stability in the operating potential window. The number of cycles useful to provide a basis to evaluate the degradation is established in 10⁴ cycles.

Reference cyclic voltammetry to investigate ECSA loss is carried out at defined intervals (after 10³, 5·10³, 10⁴ cycles). Pre and post operation physico-chemical analyses are carried out by XRD (structural), XRF (elemental), TEM and SEM-EDX (morphological), XPS (surface analysis).

2.1.1 Anode Catalyst performance

Pre-screening is carried out in liquid electrolyte by half-cell galvanostatic polarization measurements for methanol oxidation in the presence of methanol concentration ranging between 2 and 10 M. These experiments are carried out in 0.5 M H₂SO₄ /0.1 M HClO₄ by using electrodes similar to those developed for single cell testing for oxygen reduction. AC-impedance experiments for anode operation are carried out at relevant operating potentials (0.3 V RHE) in the range 1 MHz-10 mHz (10 mV r.m.s.). Overpotentials are determined at 0.125 A cm⁻² with the aim to achieve a value lower than 0.3 V IR-free at 20-60 °C as determined from IR-free Tafel plots for the methanol (2-10 M) oxidation in the range 20-60 °C (20 °C step size).

The same tests are carried out in a driven-mode operating single cell, using hydrogen feed at the cathode thus acting as counter and reference electrode. The anode is fed with methanol solution (2-10 M) and operates as working electrode. In the driven mode single cell, the operating temperature range varies from 20° to 130 °C. Overpotentials are determined at 0.125 A cm⁻² in the low temperature range with the aim to achieve a value lower than 0.3 V IR-free at 20-60 °C as determined from IR-free Tafel plots for the methanol (2-10 M) oxidation in the range 20-60 °C (20 °C step size). Whereas, in the high temperature range, overpotentials are determined at 0.5 A cm⁻² at 110-130 °C with the aim to achieve a value lower than 0.3 V IR-free as determined from IR-free Tafel plots for methanol (2-10 M) oxidation .

Reference cyclic voltammetry is carried out in the potential range 0-1.2 V RHE with a sweep rate in the range 20-150 mV s⁻¹. Determination of ECSA for PtRu-based anodes is made by CO adsorption at 0.1 V RHE and successive stripping. The ECSA is estimated from the integrated peak charge for CO stripping after subtraction of double layer charging at 0.4 V RHE [1].

The electrochemical surface area (ECSA) for Pt and Pt/Ru alloys is usually obtained respectively through hydrogen and CO/methanol stripping measurements. However, during the project the measurement of ECSA for Pt and Pt/Ru catalysts will be also performed using under-potential deposition (UPD) of copper and subsequent stripping of the Cu monolayer deposited on the nanoparticles in a standard 3-electrode cell [2].

This method can be applied to pure platinum and ruthenium and to Pt/Ru alloys with results comparable to CO stripping measurements. Electro-deposition of a metal at potentials more positive than those where that metal would deposit on its bulk phase is called under-potential deposition. The phenomenon depends on the nature of the interaction between the ad-atom and the substrate. At a potential of 0.3 V vs. RHE, a monolayer of copper deposits on both platinum, ruthenium and platinum-ruthenium alloys, although at this potential bulk deposition does not occur. After few seconds (~ 20 s) a full monolayer of copper is formed and there is no additional deposition. The deposited copper can be stripped off with a potential scan up to 1 V vs. RHE. In all tests the copper will be deposited for 2 minutes at a potential of 0.3 V from a 0.5 M H₂SO₄ solution containing 2x10⁻³ mol/l of CuSO₄. The surface area of each different electrode will be calculated from the charge under the stripping peak, corrected for the background current and assuming a stripping charge of 420 μC/cm. In fact on both platinum and ruthenium, it has been shown that the electro-sorption valency of adsorbed copper is 2 and the charge associated with the stripping of a Cu monolayer from the metal surface is 420 μC/cm.

For novel formulations, the most appropriate method to determine ECSA will be identified during the course of the project activity.

For detailed mechanistic studies additional electrochemical testing procedures to individuate the relevant electrokinetic parameters such as Tafel slope, activation energy, mass activity, specific activity at specific potentials are assessed. These consist in steady-state galvanostatic polarization curves, stability tests (both chronoamperometric and chronopotentiometric).

To get insights into the mechanism, ac-impedance spectra will be carried out at relevant operating potentials (0.1 V, 0.3V, 0.5 V RHE) in the range 1 MHz-10 mHz (10 mV r.m.s.). The series and charge transfer resistance is determined from the high frequency intercept on the real axis of the Nyquist plot and from the polarization resistances (low frequency intercept of the relevant semicircle).

2.1.2 Anode Catalyst degradation

Investigation of anode catalyst degradation in half-cell is carried out by using potentiodynamic cycling at 75 °C in 0.5 M H₂SO₄. The potential limits in these cycles are 0.1 V - 0.5 V RHE (sweep rate 20-150 mV s⁻¹) to explore anode catalyst stability in the operating potential window. The number of cycles useful to provide a basis to evaluate the degradation is established in 10⁴ cycles.

Reference cyclic voltammetry to investigate ECSA loss is carried out at defined intervals (after 10^3 , $5 \cdot 10^3$, 10^4 cycles).

In parallel, accelerated stress tests for catalyst degradation with particular reference to Ru ions dissolution are carried out by chronoamperometry at a fixed potential e.g. 0.5 V RHE representing the upper limit of the anode potential window for DMFC operation.

Pre and post operation physico-chemical analyses are carried out by XRD (structural), XRF (elemental), TEM and SEM-EDX (morphological), XPS (surface analysis).

The main protocols for electrocatalyst characterization are summarised in Table 2.

Table. 2

Protocol Category	Properties addressed	Experiment	Parameters to be determined	Screening/ Milestone addressed
Cathode performance test	Oxygen reduction reaction (ORR) Overpotential; Tafel plots	ORR steady-state galvanostatic polarizations in half cell; O ₂ feed; 20°-80°C; diluted methanol simulating cross-over (0.005 M) preferably 0.1 M HClO ₄	ORR Overpotential at 0.125-0.5 A cm ⁻² at specific catalyst loading; Tafel slope; mass activity; specific activity at relevant potentials	Pre-screening
Cathode performance test for low temperature application	Oxygen reduction reaction (ORR) overpotential Tafel plots	ORR steady-state galvanostatic polarizations in a single cell under dynamic mode operation O ₂ feed; 20°-90°C; diluted methanol simulating cross-over (0.005 M); Specific electrolyte Ionomers	ORR Overpotential at 0.125 A cm ⁻² at 60 °C at specific catalyst loading; Tafel slope; mass activity; specific activity at relevant potentials and temperatures	MS5/MS11
Cathode performance test for high temperature application	Oxygen reduction reaction (ORR) overpotential Tafel plots	ORR steady-state galvanostatic polarizations in a single cell under dynamic mode operation;	ORR Overpotential at 0.5 A cm ⁻² at 110°-130 °C at specific catalyst loading;	MS6/MS11

		O ₂ feed; 100°-140°C; diluted methanol feed simulating cross-over (0.005 M); Specific electrolyte ionomers	Tafel slope; mass activity; specific activity at relevant potentials and temperatures	
Anode performance test	Methanol oxidation reaction (MOR) overpotential Tafel plots	MOR steady-state galvanostatic polarizations in half cell Methanol (2-10 M); 20°- 80°C; 0.5 M H ₂ SO ₄ /0.1 M HClO ₄	ORR Overpotential at 0.125 -0.5 A cm ⁻² at specific catalyst loading; Tafel slope; mass activity; specific activity at relevant potentials	Pre-screening
Anode performance test for low temperature application	Methanol oxidation reaction (MOR) overpotential Tafel plots	MOR steady-state galvanostatic polarizations in a single cell under dynamic mode operation Methanol feed (2-10 M); 20°-90°C; Specific electrolyte ionomers	MOR Overpotential at 0.125 A cm ⁻² at 60 °C at specific catalyst loading; Tafel slope; mass activity; specific activity at relevant potentials and temperatures	MS5/MS11
Anode performance test for high temperature application	Methanol oxidation reaction (MOR) overpotential Tafel plots	MOR steady-state galvanostatic polarizations in a single cell under dynamic mode operation Methanol feed (2-10 M); 100°-140°C; Specific electrolyte ionomers	MOR Overpotential at 0.5 A cm ⁻² at 110°-130 °C at specific catalyst loading; Tafel slope; mass activity; specific activity at relevant potentials and temperatures	MS6/MS11

Cathode accelerated stress test	Cathode stability in the operating potential window	Electrochemical step cycles between 0.6-0.9 V RHE 0.5 M H ₂ SO ₄ and/or relevant ionomers at relevant temperatures; reference polarizations and CV at specific time intervals	Cathode performance degradation after 10 ⁴ cycles; Surface area loss.	Pre-screening/MS9
Anode accelerated stress test	Anode stability	Potential hold at 0.5 V RHE in 0.5 M H ₂ SO ₄ and/or relevant ionomers at relevant temperatures; reference polarizations and CO stripping analysis at specific time intervals	Amount of Ru ions loss after 24 hrs for PtRu based catalysts As determined by X-ray fluorescence analysis of the catalytic layer. Anode performance degradation; Surface area loss	Pre-screening/MS10

3. Catalyst loading

Catalyst loading in half-cell studies will be initially fixed to 1-2 mg cm⁻² for anode/cathode configurations and noble metal formulations in relation to portable application, whereas, it will be reduced to 0.5-1 mg cm⁻² for high temperature operation. For non noble metal formulations the most appropriate catalyst loading will be identified during the course of the project activity.

4. Further specifications

- For cathode investigation in both half cell testing in liquid electrolyte and driven mode operation, the anode will be based on a reference PtRu electrocatalyst to avoid significant activation overpotentials during testing of new developed cathodes. Similarly, for anode investigation a Pt catalyst will be used. The counter electrode, if fed by hydrogen may be assumed as reference electrode (RHE) after correction by the ohmic drop. In the half cell testing in liquid electrolyte, a reference electrode such as Hg/HgSO₄ is used. Geometrical electrode area is fixed in 2 cm² in liquid electrolyte and 5 cm² in driven mode single cell for screening of new formulations; 25-50-100 cm² for further validation.

5. Rotating disc electrode measurements

The oxygen reduction reaction (ORR) on standard Pt-based and innovative Pt-free electrocatalysts will be carried out using the rotating disk electrode (RDE) configuration in a standard 3-electrodes cell. This configuration allows to carry experiments under controlled mass transport to the electrode which is a critical factor for the ORR. The RDE measurements are carried out on the catalysts deposited on glassy-carbon disk electrodes, mounted in an interchangeable RDE holder. A Pt-wire counter-electrode and a reference electrode (separated from the working solution by a Nafion membrane to avoid anion contamination) is used in a standard three-compartment electrochemical cell. All potentials are reported in terms of the reversible hydrogen electrode (RHE) scale, calibrated before each measurement at each temperature via H₂ oxidation/reduction measurements on platinum. Oxygen reduction activities are measured at 20-80°C in 0.1 M HClO₄, for positive-going potential sweeps between 0 and 1.0 V versus RHE at low sweep rates (5 and 20 mV/s), in order to minimize the interference from capacitive currents. Measured currents were mass-transport corrected in order to determine mass and specific activities. Further details of electrode preparation and testing are reported in the literature [3, 4]. The experiments will be performed also in presence of diluted methanol (0.005 M) simulating the cross-over. Figure 2 shows the experimental apparatus for RDE measurements.

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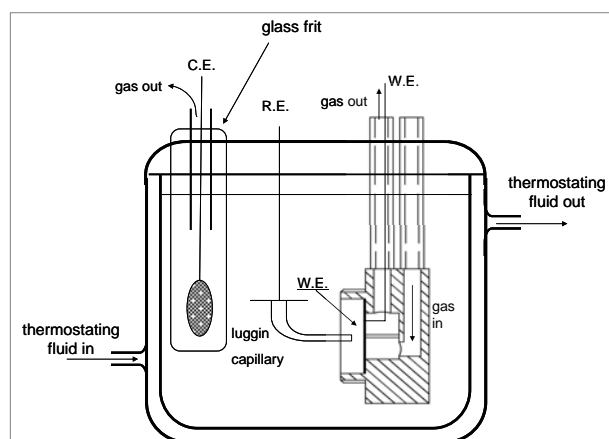


Fig. 1 Apparatus for half –cell studies



Figure 2 Apparatus for rotating disk electrode measurements.