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Experimental approach for the study of SOFC cathodes

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The suitability of impedance measurements in Solid Oxide Fuel Cells (SOFCs) is an important concern, especially in case of measuring separately the behaviour of one of the electrode when an overvoltage is applied. In this case a thin electrolyte-supported cell with the RE (Reference Electrode) coplanar with the WE (Working Electrode) is experimentally convenient, but many authors highlighted that incorrect results can be obtained if an inappropriate geometric configuration is used. In this work LSM cathodes ($(La_{0.8}Sr_{0.2})MnO_{3-x}$) were investigated in a Yttria-stabilised Zirconia (YSZ) electrolyte-supported cell, using an electrolyte 3 mm thick. Two types of cells were prepared: the first (Cell1) according to the geometric requirements suggested in literature: little WE (diameter 3 mm) aligned to the CE (Counter Electrode) and with equal R_{pol}(polarisation resistance) and time constant; RE co-planar around the WE and placed at a distance greater than three-electrolyte thicknesses from the WE; the second one (Cell2) equal to Cell1 but with a bigger WE (diameter 8 mm). Impedance measurements were carried out both in two- and three-electrode configuration, at OCV (Open Circuit Voltage) and under applied overpotentials. A preliminary comparison between the results extracted from Cell2 at two- and three- electrodes confirms that a thick electrolyte allows extracting suitable three-electrode impedance results in case of OCV and small overpotentials. On the other side, when an overpotential over 0.2 V is applied, a comparison between Cell1 and Cell2 gives quite different results. The investigation here presented considers also an experimental approach useful for the comprehension of the main phenomena governing the kinetic of the process.

Keywords: Solid oxide fuel cells, impedance spectroscopy, electrode kinetic

INTRODUCTION

DC and AC electrochemical techniques are one of the tools necessary for the study of Solid Oxide Fuel Cells. AC measurements are normally performed on experimental cells and cell stacks, which reflects the real features of the electrochemical system, or are carried out on simplified systems, that allow the separated study of one component of the system. In this case a thin electrolyte-supported cell with the RE coplanar with the WE is experimentally convenient, but many authors highlighted that incorrect AC impedance results can be obtained if an inappropriate geometric configuration is used [1,2,3].

Moreover, the quality of the impedance data is not only related to the geometry of the system, but also to the procedure applied during the testing stage. It is recommended that before systematic impedance investigation the linearity of the system be checked, in order to choose the perturbation amplitude which vouches for the linearity of the system and at the same time the highest quality of the impedance spectra considering also that the maximum permissible amplitude of a perturbating signal is smaller at low frequencies than at high frequencies. This approach should be applied particularly when low impedance systems like SOFCs are studied. The low impedance of the system is a critical factor and can be improved with small cell geometries. The obtained data gain quality if the inductance of the cell rig is extracted under the same conditions of the cell measurements (temperature, cables looping) and is then subtracted to the cell frequency dispersion. Cell geometry remains anyway a crucial point.

In this paper a simplified cathode made of only a porous LSM layer applied on YSZ dense and

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thick electrolyte (3mm) is considered. The choice of such a cathode is due to the fact that: i) this electrocatalyst has a real application on SOFCs, ii) it posses a negligible ionic conductivity with respect to the electronic conductivity, iii) it is still not yet fully clear the mechanism of oxygen reduction at a SOFC cathode.

Two types of cells were prepared. The first (Cell1), according to the geometric requirements suggested in literature, having little working electrode (WE, diameter 3 mm) aligned to the counter electrode (CE) and with equal R_{pol} and time constant. The reference electrode (RE) co-planar around the WE is placed at a distance greater than three-electrolyte thicknesses from the WE. The second type of cell (Cell2) equal to Cell1 but with a bigger WE (diameter 8 mm).

Impedance measurements were carried out both in two- and three-electrode configuration, at OCV and under different applied overpotentials.

This research has the aim to stress some of the most important criteria to be applied when impedance measurements are performed in order to have reliable experimental data to be used for the interpretation of the electrode kinetic. Furthermore, an attempt to understand the main phenomena governing the kinetic of the oxygen reduction on LSM pure cathodes is presented.

EXPERIMENTAL

The supporting electrolytes were produced by uniaxial pressing the YSZ powders (TZ-8Y Tosoh) and sintering at 1500°C for 1h. The electrolyte dye was carefully designed in order to obtain pellets with a reproducible diameter of 35 mm and 3 mm in thickness after sintering.

For the electrodes deposition a screen printing ink was produced adding to the $(La_{0.8}Sr_{0.2})MnO_{3-x}$ powder (LSM20-P Fuelcellmaterials.com) the proper amount of solvent, deflocculant and binder following the procedure reported by Sanson et al [4].

Thick films were screen printed (squeegee speed = 0.12 m/s, squeegee load = 4.5 kgF, snap off = 0.9 mm; AUR’EL 900, AUR’EL Automation S.p.A., Italy) onto the YSZ pellets and dried at 80°C x 30’ into an infrared furnace. Suitable masks were used to print the two types of cells (Cell1 and Cell2), according to the desired geometries (Cell1: WE and CE diameter 3 mm; Cell2: WE and CE diameter 8 mm).

The as-deposited films were finally sintered at temperatures of 1050 °C and 1150 °C for 2h, producing Cell1-type at the two different sintering conditions and Cell2-type at the only 1050 °C sintering condition.

The cells were placed inside an in-lab constructed test station for the electrochemical investigation. The system was heated at a rate of 0.9 °C min^{-1} up to testing temperature (700-800°C).

The electrochemical measurements were carried out in a two- and three-probe configuration, using a potentiostat coupled to a frequency response analyser (Autolab PGSTAT302N). During the testing procedure, the cathode was exposed to the ambient atmosphere or fed with pure oxygen. Impedance measurements at open circuit voltage (OCV) in a frequency range of 10^6 to 10^{-1} Hz were carried out in potentiostatic mode. Before starting any systematic analysis, the linearity of the system response was checked, ranging the voltage perturbation amplitude from 5 to 50 mV. Short circuit measurements were performed under the same conditions of the systematic analysis and the obtained data were subtracted to the impedance spectra for the inductance correction.

A microstructure investigation of cells both before and after the testing was carried out by SEM (LEO1450 VP Scanning Electron Microscope) and EDS microanalysis (INCA Energy 300, Oxford Instruments Analytical).

RESULTS

The first set of experimental tests was focused on the cell with a typical electrode diameter of 8 mm. This size is quite commonly used in literature and in studies performed in our Lab [5, 6]. The first check to verify the measurement reliability was the comparison of the results extracted at two- and there-electrode configuration. Also in the latter case the cell was symmetric, since the two opposite electrodes were prepared according to the same formulation and shape. As mentioned in the experimental section, a careful preparation of the cell was paid as for the alignment, size, thickness, and structure of the electrodes. Typical inductance corrected Nyquist plots are reported in Fig 1.

The spectra show a depressed capacitive loop, which suggests the presence of at least two different time constants, in line with the complex path for the oxygen process. The spectra allow us to extract, with a good precision, the value of the total resistance of the capacitive loop as the difference between the intercept of the frequency dispersion with the real axis at low and high frequencies (polarization resistance, R_{pol}).

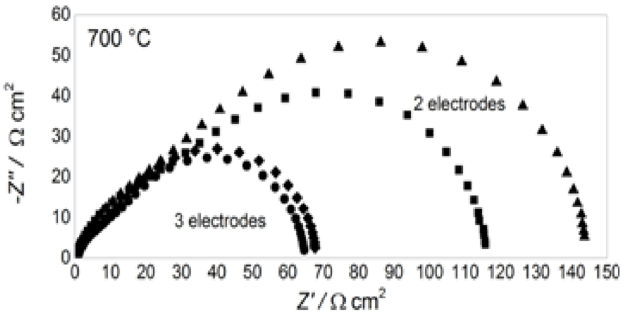

Fig. 1. Impedance spectra of Cell1 at OCV in two- and three-electrode configuration $p(O_2)$ = 0.21 atm (triangle and rhombus), $p(O_2)$ = 1 atm (square and circle). Operating conditions: 700 °C.

This parameter includes all the resistances experienced by the overall process, which takes place at the electrode under investigation, and it is always considered in the studies of the reaction kinetics. In order to ensure the reliability of the results, the same value of the total resistance has to be extracted from the same electrode in both cell configurations. Discrepancies due to different geometry and/or structure of the two opposite electrodes give rise to variations of the single electrode total resistance, which is estimated singularly and totally in the three- and in the two-electrode configuration, respectively [2].

A general view of this aspect is given in Fig 2 through the comparison of the R_{pol} for Cell2 in three-electrode and half of the total resistance in two-electrode configuration, at different operating conditions. The values obtained show a very good symmetry of the system confirming what was already observed through the morphological analysis. In fact both electrodes possess very close polarization resistance. In addition, the results at open circuit voltage and small overpotential (0.1 V) suggest that EIS measurements are reliable in the three-electrode configuration even with a RE placed at a limited distance from the WE.

The comparison of the results obtained from Cell2 (ΦWE = 8 mm) and Cell1 (ΦWE = 3 mm), extracted in the 3-electrode configuration, is reported at different overpotentials in Fig. 3. It is highlighted a good agreement of the results obtained at low polarisations (OCV to 0.2 V), while for high polarisations of the electrode (0.3 V and 0.4 V) the two geometries of the same sintering electrode do not match any longer. The increased distance of the RE from the WE is the only difference of Cell1 with respect to Cell2. According to the studies available in literature [7, 8] the reference electrode of Cell2 is polarised when high overpotentials are applied, consequently poor reliability of the measurement data have to be considered. Measurements on cells with the same apparent geometry but different porosity, which indirectly means different particle size/electrode specific area and TPB length, have been performed, by preparing cells of type 1 with two different sintering process of the LSM electrode. According to previous experiences [9, 10, 11, 12] the electrode sintering at 1050 and 1150°C produces a good variation of the electrode porosity, 50% and 30% respectively, and average particle size, 0.7 µm and 2 µm respectively. Electrode porosity and mean particle size were evaluated by image analysis of SEM micrographies.

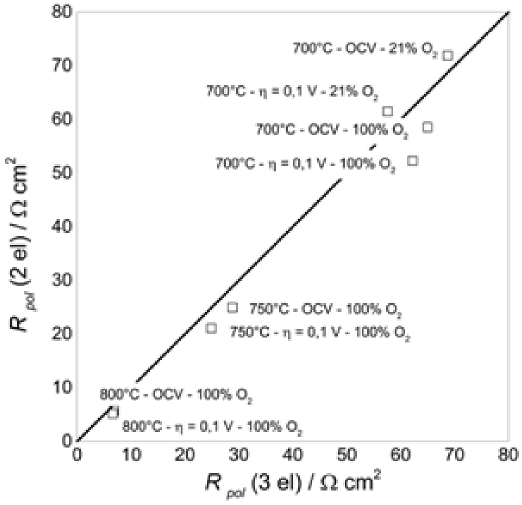

Fig. 2. Comparison between R_{pol} extracted in three-electrode configuration and half of the total R_{pol} resistance in two-electrode configuration, for Cell2. Operating conditions reported on the picture.

The total R_{pol} has been extracted from the impedance measurements on both systems with a three-electrode configuration (Cell1 type) as a function of overpotential and are reported in Fig 4. These results highlight a remarkable difference of the process kinetic in the two samples at OCV. Such difference decreases as the overpotential increases. About the electrode sintering temperature, two main aspects have to be considered and they are: i) a relatively small particle size and high electrode porosity produce a structure with a high LSM active surface per unit volume, useful for adsorption and diffusion phenomena; ii) a relatively small particle size and high sample porosity produce an improved TPB length at the electrolyte interface, which enhances charge transfer.

In order to find a direction between these possibilities that both enhance and control the overall process, the plot of $\ln(R_{\mathrm{pol}})^{-1}$ against the overpotential [13] can be used to check if the typical Butler-Volmer behaviour for charge transfer controlled reaction hold in this case. A linear trend of the experimental data cannot be considered and a credit to the first hypothesis of adsorption and mass transport of the electroactive species as controlling steps looks more suitable (Fig 5).

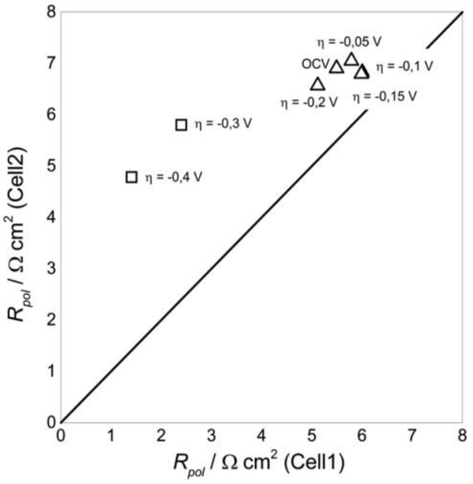

Fig. 3. Comparison of the results obtained from Cell1 and Cell2 in the three-electrode configuration at different overpotentials (triangle OCV ÷ 0.2 V; square 0.3 V ÷ 0.4 V) at 800 °C and $p(O_2)$ = 1 atm. Data corrected with the geometric area of the electrodes.

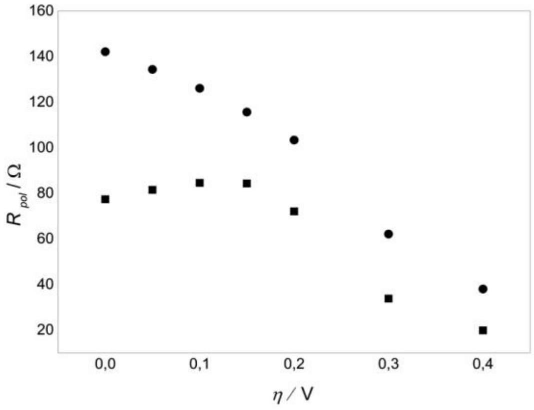

Fig. 4. R_{pol} for Cell1 with LSM electrode sintered at 1050 °C (square) and 1150 °C (circle) at different overpotentials (800°C and $p(O_2)$ = 1 atm).

The role of adsorption and transfer phenomena in the electrode reaction can be faced with the analysis of the impedance spectra. Nyquistplots of Cell1 (Fig. 6) shows that both at OCV andunder WE polarisation the high frequency part of the plot contains a component related to linear diffusion in a homogeneous layer with finite thickness [14]. The quantification of this phenomenon can be performed with the aid of data fitting with equivalent circuits models [15] or with other impedance analysis techniques, like Differential Impedance Analysis [14, 16, 17]. It has to be pointed out that the use of equivalent circuits risks to be speculative if a preliminary basic analysis of the data, which individuate the possible components of the circuit, is not performed.

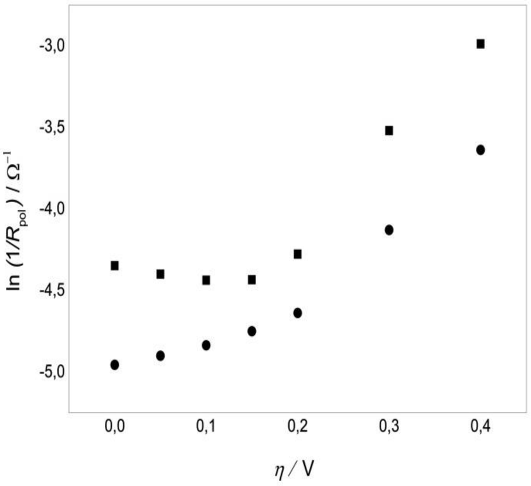

Fig. 5. Trend of $\ln(R_{pol})^{-1}$ versus overpotential at 800°C and $p(O_2)$ = 1atm, square sample sintered at 1050 °C, circle sample sintered at 1150 °C.

Good fitting results of the obtained experimental data are already available with a simple typical Voigt model, used in solid-state electrochemical systems. This takes into account of a two time constants equivalent circuit: the low frequency part of the spectra is described with an R/CPE (Resistance-Constant Phase Element, CPE) term and recalls a transport phenomenon, while the high frequency partwith an RC (Resistance-Capacitance) in series with the previous term and suitably related tocharge transfer. An example of fitting is presented in Fig 7.

The low frequency part of the spectra recalls a transport phenomenon, while the high frequency part is well described by a RC parallel, suitably connected to the charge transfer. The low frequency mesh (R_2Q) ascribed to transport phenomena shows a strong R_2 dependence on the applied overpotential (Fig 8).

At OCV the increasing temperature improves remarkably the kinetic of the process. Considering that at OCV diffusion is the main driving force for mass transport and that the diffusion coefficient in the Fick's law is strongly dependent on temperature [18] the gas diffusion mechanism can be related to the increase of $1/R_2$ with the operating temperature.

At high overpotential $1/R_2$ shows a further improvement with respect OCV. This is especially observed at 700 °C. If the transport mechanism would be controlled only by the gas diffusion the

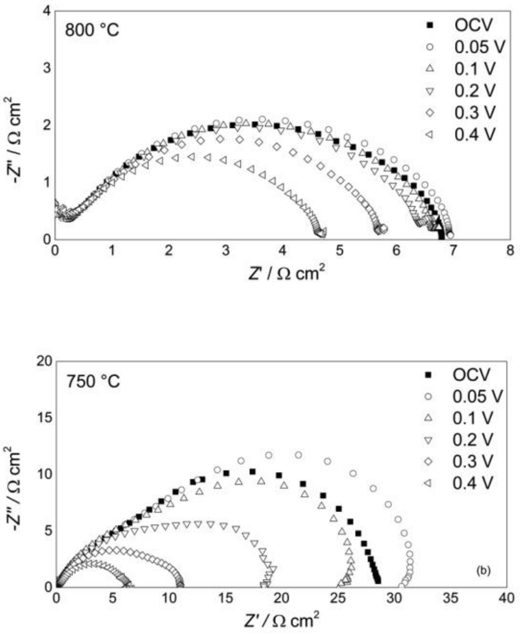

Fig. 6. Nyquist plots of Cell2 at $p(O_2)$= 1 atm, 800°C (a), e 750°C (b), at different cathodic overpotentials.

slope of these curves should not change. Then, when overpotential increases a further transport phenomenon should be considered, which is more important where diffusion is slower (700 °C). Migration of the electroactive species through the subsurface or even inside the bulk of the LSM could be recalled. This supports the mechanisms that foresee the formation of an intermediate charged species (O^{2-} or O^{-}) adsorbed on the LSM surface, with following incorporation inside the LSM oxygen vacancies, according to literature [19, 20, 21, 22]. This is also in agreement with the values of polarisation resistance at 800°C presented in Fig 4; in fact, at OCV the amount of active site is high in the most porous electrode (sintered at 1050°C), which has available a wide path for surface transport of adsorbed oxygen ions. Under polarisation the transport of oxygen ions is enhanced also into the LSM bulk. Then, the porosity of the electrode does not play a relevant role, providing oxygen gas at the active site for adsorption and first charge transfer, and the total polarisation resistance detected in the differently porous electrodes are getting closer.

CONCLUSIONS

This research has the aim of stressing some of the most important criteria to be applied when impedance measurements are performed, in order to have reliable experimental data to be used for the interpretation of the electrode kinetic. The system investigated in this study (pure LSM SOFC cathode) was chosen since it has a real application; moreover, it constitutes a simplified but meaningful configuration with respect tocomposite electrodes and, finally, because a clear understanding of the electrochemical oxygen reduction is not yet been addressed. The presented approach shows how cell

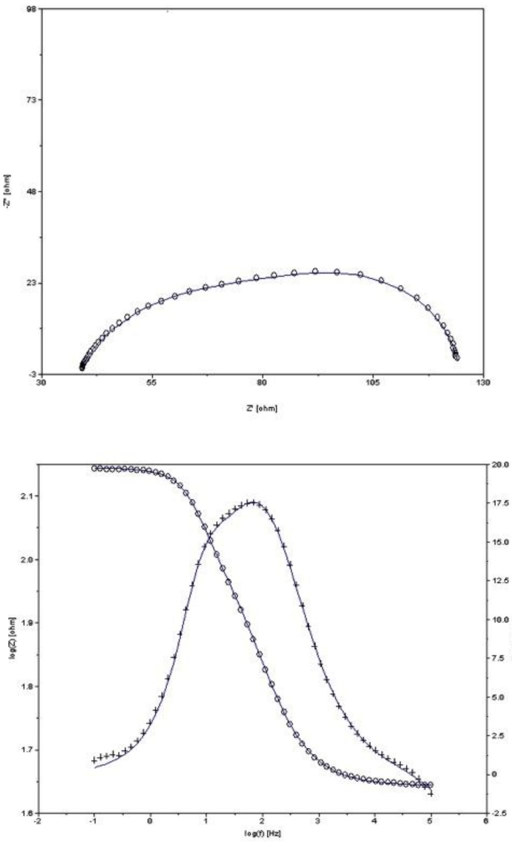

Fig 7. Fitting of the experimental data of Cell2 at 750°C, $p(O_2)$ = 1 atm, two-electrodes configuration, by an $R_1(R_2CPE)(R_3C)$ circuit at OCV (R_1 = 39.5 Ω, R_2 = 53.5 Ω, Y_0 = 0.27 10^{-3}, n = 0.73, R_3 = 46.5 Ω, C = 0.5 mF).

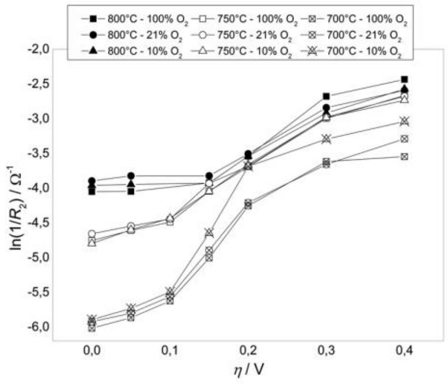

Fig. 8. Low frequency part resistance (R_2) plotted versus overpotential, at different operating temperature and different $p(O_2)$.

geometry, cell configuration, electrode porosity and operating conditions (temperature, reactant concentration and overpotential) can be managed to have sensitiveness of the phenomena controlling the overall process. However, the match between the experimental approach, presented in this paper, with a theoretical study, able to simulate the impedance spectra on the basis of a physically consistent model, is the target to achieve a comprehensive analysis of the system [23, 24]. A theoretical approach based on:

- a simplified mathematical reconstruction of the system based on the microscopic observation of the real structure of the electrode and interfaces;
- the quantification of the effective properties (diffusivity, conductivity, tortuosity, TPB length);
- the application of a kinetic model [25, 26] based on the physical processes with related boundary conditions;
- is under study and will be the object of further communications.

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ЕКСПЕРИМЕНТАЛЕН ПОДХОД ПРИ ИЗСЛЕДВАНЕ НА КАТОДИ ЗА ТВЪРДООКСИДНИ ГОРИВНИ КЛЕТКИ (SOFC)

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(Резюме)

Пригодността на импедансните измервания натвърдооксидни горивни клетки (SOFC) е основен проблем, особено в случайте на разделно измерване на поведението на един от електродите, когато се прилага свръхнапрежение.В този случай тънка клетка с електролит за опора и CE(сравнителен електрод) копланарно с РЕ(работенелектрод) е експериментално удобна, но много автори изтъкват, че могат да се получат погрешни резултати, ако се използва неподходяща геометрична конфигурация.В тази работа LSM катоди ((La0.8Sr0.2) MnO3-x) бяха изследвани вклетка с итриевостабилизиран циркониев (YSZ)електролит за опора,с дебелина 3 мм. Бяха получени два вида клетки: първата (Клетка1) съгласно геометричните изисквания посочени в литературата: малък РЕ (диаметър 3 мм) в права линия спрямо противо електрода (ПЕ) и с равни Rpol (поляризационно съпротивление) и времеконстанта; СЕ се ориентира копланарно около РЕ и се поставя на разстояние по-голямо от три електролитни дебелини от РЕ; втората (Клетка2) е равна на Клетка1, но с по-голям диаметър РЕ(8 мм). Бяха осъществени импедансни измервания при дву- и три- електродни конфигурации, при напрежение на отворена верига (ОСВ) и при прилагани свръхнапрежения. Предварителното сравнение на резултатите, получениза Клетка2 при дву- и три- електродната клетка потвърждава, че един дебел електролит позволява да бъдат получавани подходящи импедансни резултати за трите електрода в случаитепри напрежение на отворена верига и малки свръхпотенциали. От друга страна, когато се приложи свръхнапрежение от над 0.2 V, сравнението между Клетка1 и Клетка2 дава трърде различни резултати. Представенитетук изследвания разглеждат също така експериментален подход, полезен за разбирането на основните явления които управляват кинетиката на процесите.