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Project

Production oriented process engineering for establishing reliable SOFC cell and stack manufacturing

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ZUSAMMENFASSUNG

HTceramix's production technology has been validated on the laboratory scale, but frequently required the intervention of scientific personnel in several steps. The objective of this project is to adapt the SOFC production techniques to the requirements of pilot production environment, i.e. PhD independent processes fulfilling minimum levels of reproducibility. Processes have been stabilized, reproducibility has reached a minimum level and several processes have been scaled up.

An experienced process engineer has analyzed and adapted the laboratory manufacturing route to achieve process stability and reproducibility on pilot manufacturing scale. Critical steps that had to be adapted were powder processing, tape casting and sintering. Also the extent of use and losses of expensive raw materials have been reduced.

Considerable efforts where invested in formalizing best practices on laboratory scale to define a base-line for continuous production. External supply of powders allowed stabilizing the product, though on a lower performance level. A quality chain has been put in place for all manufacturing steps. The project has reached its goal in terms of quality assurance, product traceability and production capacity.

Projektziele

The objective of this project is to adapt HTceramix's low cost SOFC production techniques for cells and SOFConnex™ to the requirements of a pilot production environment. The goal is to stabilize the processes to improve reproducibility, identify relevant quality control parameters and to implement process control protocols for all manufacturing steps. Thereafter, the remaining process and equipment bottlenecks will be identified, processes adapted and new equipment designed and sourced in order to enable the pilot production line to reach a capacity of 200 pcs/week.

The expected results are process control protocols with clear quality control parameters integrated on the current 20pcs/week laboratory line. Thereafter, processes and equipments will be developed and validated with the aim to reach a production capacity of 200pcs/week.

Durchgeführte Arbeiten und erreichte Ergebnisse

Task 1: Transfer of process control protocols to the production line

Detailed recipes for each optimized process steps (more than 45 production steps are necessary to produce one repeat element) have been formalized on Excel sheets and serve as a base for production tracking and implementation of quality control parameters.

1) For the manufacture of repeat elements the actual state of the art has been transferred from the research and development laboratory to the production plant in Yverdon.

   In order to fulfil the production requirements, all methodology has been tested on site, modified if necessary and validated. With the participation of R&D, all procedures are in continuous improvement.

2) All established protocols are submitted to periodical revision in order to implement the improvements in documentation.

3) Optimization strategy has been applied in evaluation of process steps and raw materials availability.

   For example, the manufacture of nickel oxide from soluble nickel salt (nickel nitrate) has been abandoned because the process was too expensive regarding recovery, waste management and availability of this product on the market.

Task 2: Definition of QC parameters

a) For powders:

1) To achieve reproducible production, NiO was sourced from an external supplier. This new raw materials still has been validated on the level of its impact to the mechanical stability of the cells. Cells are less reliable on the mechanical level, but the products are uniform within and between several batches.

   One supplier has been chosen for the nickel oxide. Specifications given by this supplier is in accordance with our product quality. Nevertheless we continue to evaluate this raw material from other suppliers, with the aim to regain the former mechanical stability.

2) Perovskite powders are obtained from external partners. Quality control of new batches represents currently a bottle neck on the level of the infrastructure.

3) Continuous evaluation of products is performed through analytical measurements (ICP, XRF, PSD, BET) and by in situ electrochemical tests.

   The electrochemical method has been improved (reproducibility) in order to evaluate properly the perovskite powders used for cathode and current collection cathode layers. Production plants visits and meetings are planned and held on regular basis with supplier in order to improve traceability and reproducibility.

4) Contacts have been established with different suppliers in order to enlarge the availability of these raw materials, the dependency on one supplier may be problematic. It is also useful to test different perovskites in order to benefit from possible improvements of such products.

   Specification sheets are in improvement in accordance with the suppliers and our needs. We are also in contact with potential suppliers who are starting in production of perovskite powders in order to evaluate the potential of alternative materials.

b) For slurries:

1) Preparation of anode slurry and current collection slurry

   Milling conditions are controlled in order to be reproducible.

   Particular efforts have been made to ensure constant properties of the slip for the tape casting. Viscosity is systematically measured during production. The viscosimeter is calibrated regularly with a reference viscosimeter. Specific gravity is measured at lower frequency to control total content of solid before casting.

   In order to eliminate agglomerates on the tape, the slurry is systematically filtered; this step gives successful results.

2) Preparation of electrolyte slurry

   Milling conditions are controlled in order to be reproducible. Degassing of the slip is performed at constant and reproducible conditions. Viscosity is systematically measured on line. The viscosimeter is calibrated regularly with a reference viscosimeter

3) Preparation of current collection slurry

   As the above-mentioned slurries, the characteristics of this product are controlled but at less extend because less critical.

4) Preparation of screen printing ink

   Screen printing is critical in cathode performances; therefore parameters must be well controlled. Characteristics of screen printing ink like total solids content and viscosity are controlled. The measurement of total solids permits for example to check the cathode layer thickness on line by gravimetry.

5) Preparation of SOFConnex™ cathode and anode slurry.

   Since May the SOFConnex™ are manufactured in Yverdon. The anode paste and the cathode paste have been improved in order to provide products matching with the requirement of people stacking elements. Softness and dimensional characteristics have been improved. The established procedures need further improvement, the goal is to narrow down specifications in order to minimize production variations.

c) For the tape:

1) Electrolyte casting

   Trials have been performed by peristaltic pump continuous feeding in order to improve casting uniformity and to permit larger production volume. Results are promising, fine tun-

ing is planned. This technique also permits to reduce manpower during casting (1 people instead of 3).
Electrolyte thickness measurement using microscope depth of field is not used anymore because it is not reliable enough. SEM measurements are performed on a regular basis. An on-line electrolyte thickness measurement using photometric technique is under development. This technique will be validated by SEM comparative measurements

2) Anode casting

Anode support height controlled by Dr. Blade which is positioned with micrometric screws. As for electrolyte, the anode casting can be performed by continuous feeding using a peristaltic pump. This technique permits a more constant tape thickness and less manpower. Viscosity is now systematically measured and total solid content is under control. Density is measured on regular basis but not for all batches.

A systematic thickness data treatment permitted to identify critical point in the tape casting process

3) Drying

Air Humidity and temperature are measured and maintained at required level.

Some problems in humidity control were observed during this summer. It was possible to increase humidity but not to reduce; now the drying room is equipped with a system of dehumidification. Drying conditions now permit to ensure reproducible and constant cells dimensions. A better control in drying time will be implemented in order to avoid corrections in tape cutting step.

d) For half-cells and cells:

1) Sintering

The furnace temperature has been controlled but it is necessary to perform it on a regular basis (autocontrol). It is also important to evaluate the temperature gradient

2) Shape control

Statistical data have been collected and treated systematically. They show the improvements in cells shape.

3) Mechanical properties

Mechanical tests have been performed on cells and SOFConnex™. They can demonstrate that some mechanical problems remain. The use of pressure sensitive paper permits to identify the critical pressure points. Further improvements will be planned in the level of R&D.

e) For SOFConnex™:

1) Deposition on cell

Since May the SOFConnex™ cathode and anode are manufactured in Yverdon.

During this period the following improvements have been done:

- use of alignment rack permitting a more accurate manufacture
- develop a system for sealing stamping
- modify recipes in order to improve reliability and softness

f) Summing-up:

	Process parameters	Control parameter/check	Adjustment / Remedy	Physical process value	Physical result value
Powder	pH/titration/T	MEB/BET/Optical microscope	add base or acid	**pH X**, conc. oxalate X M, TX°C	aspect
Dispersion	liquidity threshold	PSD (particle size distribution)	ball milling time	l. t. x gr/gr	**d 50 X6 um**
Slurry	T/maturity/viscosity electrolyte/anode		dilution or additional polymer	T X°C/ maturity X min/X **mPa*s**/X mPa*s	
Casting	Pressure on thin layer	Thickness of casted layers, gravimetric or light transmission control	adjust caster	Constant pressure, X **N**	X um /X um
Drying	humidity/T		controlled atmosphere	**rh X%**, X°C	
Sintering		shrinkage	adjust cutting geometry	X%	
Cathode ink	viscosity		adjust viscosity, adjust screen printing machine and number of layers	**X mPa*s**	
Screen printing	Screen distance, blade speed	Layer thickness	regulate blades and speed	X mm	X um

The next step is to replace some methods which are tricky, time consuming and expensive by simpler on-line methods, for example replace electrolyte layer control by SEM by photometrical measurement.

Task 3: Stabilise critical processes

a) Third party supply:

The preparation of NiO was abandoned because not profitable comparing to the availability of this product in the market. However the choice of a reliable supplier was an important task. The NiO used now is not obtained on the same way as we did, nevertheless it is possible to ask to one supplier to prepare this product using the same process (oxalate way).

b) Established protocols:

All procedures are frozen. Nevertheless changes must be done constantly because the specifications for some raw materials are too broad and adaptations are necessary or because improvements in product or process can be implemented.

c) Critical production parameters:

Anode thickness is under control using a function correlating doctor blade height with anode thickness. Verification of the function is performed on regular basis.

d) Communication with R&D and external technical advisors:

To optimize screen printing of cathode characteristics of printing ink must be improved. We are requesting R&D to perform tests in order to optimize the production in accordance to our technical and QA needs. Close feedback is organized. A screen printing specialist has been contacted in order to optimize our process.

Task 4+5: Development of adapted processes (incl. QC) and design and source of new equipment for the pilot production line (200 pcs/week)

a) Tape casting:

The tape casting needed 3 people because all operation was done manually, for example slurry feeding, level control, plates feeding. More, the manual operations cannot ensure a constant quality.
Now the tape casting machine is provided by a roller table for the collection of the coated plates; this permits to spare operators time and avoid any casting perturbation due to the plates unloading.

In order to ensure a constant tape casting, the slurry feeding is performed using peristaltic pumps provided by a level control system. This technological development has been done internally.

b) Tape drying:

Improvements in drying conditions have been obtained by implementing a system to control humidity and temperature. Drying time is controlled but not optimized. Presence of dusts is not the major issue in quality of the tape, therefore the drying room is not yet equipped with filtered air. Cupboards with filtered air are considered as an alternative.

c) Cell cutting:

The cell cutting is now systematically performed on the plotter Mimaki CF-0912-2. This machine permits to obtain cells of any shape and fulfil any costumer request. Size limits are given by the casting conditions (max 120 mm width after sintering) and the oven dimensions (max 240 mm length after sintering).

Because the tape drying conditions are not fully controlled (drying time) it is necessary to set cutting dimensions for each batch.

d) Sintering:

At the present time, the furnace capacity is the principal bottle neck of our pilot production plant. For 82 x 82 mm elements, the batch size is maximum 30 units because the dimensions of the alumina plates are not fully adapted. By replacing these plates by 250 x 375 mm plates, it is possible to increase the batch size to 132 elements (82 x 82 mm). This way has two advantages, first to permit to fulfill the objective by reaching the production volume of 200 elements per week and second to reduce the run cost per cell of the furnace.

e) Screen printing:

The semi-automatic screen printing permits to coat about 30 elements per hour. In general, one layer is enough to reach the thickness for cathode and current collection cathode. Therefore this step is not a bottle neck and a further automation is not necessary for the close future.

The screen printing was the source of important production losses due to elements breakage. Modifications on the vacuum table (rubber layer) and a better setting of the machine eliminates this problem.

In order to obtain a reproducible operation, the viscosity of the printing ink is systematically measured.

The on-line control of the cathode thickness is being established by gravimetry; the control of this measurement will be performed by SEM.

f) SOFConnex™ production:

SOFConnex™ production came later but now the production plant in Yverdon can fulfil the demand in parallel with the production of the elements. The new casting tools developed by R&D have been successfully implemented. Nevertheless improvements are to be expected for the next step.

g) Summing-up:

1) Production goals
   (20 cells per week) have not only been reached but exceeded (45 cells per week), the planning of the next step has been accomplished. Production infrastructure is gradually modified in order to reach 200 cells per week before end 2004.
2) Resources optimization
   Production equipment is also designed in order to reduce the production costs and increase quality. Technological awareness and R&D interaction is expected to be a useful tool.

Task 6+7: Installation of new equipment and validation in the pilot production line and transfer of new processes to the pilot production line

In order to reach the production volumes planned in the objectives of the end of year 2004 (200 cells per week), studies have been started for the design of slurry production and tape casting. This infrastructure is based on a 10 liter glass reactor with integrated heating system which can directly feed the tape casting by using peristaltic pumps

Nationale Zusammenarbeit

This project is closely related to Pilot manufacturing of Solid Oxide Fuel Cells (SOFC) stacks and CTI project 6649.3 IWS-IW with EPFL and EMPA on the up-scale of SOFC stacks. It translates the requirement of increased and controlled production necessary for further up-scale of HTceramix's stack technology.

Internationale Zusammenarbeit

Procedures and protocols established serve as base for the EU integrated project „Real-SOFC" coordinated by FZ Jülich. Reference cells and stacks are delivered to project partners for testing and evaluation. The project has started in February 2004.

Bewertung 2004 und Ausblick 2005

The formalisation and establishment of production procedures has taken more time than anticipated and required intensive discussions with all people involved on the different levels. This process has clearly been beneficial to all people involved, as they were confronted with new requirements coming from a production philosophy instead of the R&D approach.

A quality and process control system has been implemented. Statistical data is collected systematically on all production batches; this data have already allowed identifying systematic errors in the production line, and it is expected that further exploitation of these data will further help to improve product stability.

In terms of production, the goals have been reached as follows:

- process steps monitored: better reliability, constant quality
- process capacity increased: higher production volume
- safety and environment: from conscience to practical measures

Further to be improved:

- technological awareness
- feedback with R&D activities, for steady product improvement

Referenzen

Ordonnance féd. Sur la protection des eaux, RS 814.201