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Degradation and stability of nanostructured energy devices

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A B S T R A C T

Nanomaterials can be employed in a variety of energy technologies to improve performance, reduce costs, and open up new applications such as microelectronics. The necessary functionalities for the energy processes (e.g. energy conversion or energy storage) are achieved through organizing these materials into complex nanostructures combined with supporting substances to complete these processes. Key functionalities accomplished in this way often include charge transfer processes. The stability of the nano-energy devices is a key factor affecting both their technical and economic viability. In this paper we discuss procedures for identifying degradation phenomena in nano-energy devices and present results from stability studies of metal oxide-based nanomaterials for dye-sensitized solar cells (DSSC) and ceramic fuel cells (CFC) relevant to microelectronics. DSSC stability study is based on TiO_2 nanostructure and CFC is based on samarium doped ceria (SDC)/carbonate nanocomposite. Analyses included morphological and electrochemical characterization. Degradation had a major impact on the charge transfer processes and on the overall energy conversion efficiency through the material interfaces. As DSSC and SDC-nanocomposite fuel cell are electrochemical devices, ion mobility linked to side reactions that weakens the original redox-reactions were found, in particular through the electrolyte, but also on material interfaces (e.g. electrode–electrolyte, core–shell particle interface) where catalytic activity is an important performance enhancing factor. When scaling up materials to the energy device level, the manufacturing method itself may also cause instabilities in the nanostructures.

1. Introduction

New energy technologies are not only relevant for mitigating the large global energy-climate problems, but they also provide solutions in the microelectronic scale. In particular, when combined with nanomaterials and nanotechnology, new energy device architectures are emerging for energy harvesting, powering small electronic applications, integrated design, etc. [1].

There are a large number of energy applications emerging from nanotechnology such as solar cells, fuel cells, Li-ion batteries, etc., all having in common novel or improved properties (e.g. catalytic, electric, optic, ionic properties) brought about by using various nanostructured materials due to their large specific surface area. In solar cells, nanostructured TiO_2 materials for dye sensitized solar cells (DSSCs) have received much interest also for microelectronic applications as the cell can easily be integrated on applications such as RF-tags, but also in varying size. The DSSC cells gain in performance compared to traditional Si-cells in low radiation indoor conditions [2]. Another interesting technology is nanocomposite-based fuel cells, which could be manufactured as a homogenous one-layer [3]. Both technologies can be manufactured as thin layers also providing flexible structures. Advanced nanomaterials helps also to improve performance: For instance, we have demonstrated a flexible counter electrode (CE) based on single walled carbon nanotubes (SWCNT) as an alternative to expensive ITO and Pt CE for a DSSC [4]. By electropolymerization of poly(3,4-ethylenedioxythiophene) (PEDOT) on SWCNT film, an efficiency of 4% was achieved by DSSC using PEDOT–SWCNT CE, which is comparable to the cell using Pt-ITO CE. Through advanced material synthesis [5], improved ionic conductivity of ceria-based nanocomposites has enabled to produce low-temperature ceramic fuel cells (LTCFC) with power densities around 0.5 W/cm^2 at 600 °C which is well below temperatures used in the SOFC-fuel cells. The freeze drying method used [5] is able not only to maintain the small particle sizes in composite, but also control the carbonate composition precisely which helps to tailor-made required nanostructures.

Though the performance of the nano-energy devices demonstrated above is highly promising in view of practical and microelectronics applications, the life-time performance will be of outmost importance for their commercialization, which has not

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received adequate attention yet. Namely, nanostructured materials may be quite unstable under thermal or light conditions due to their high surface energy leading to severe grain growth, which may result in degradation of the device performance [6]. Therefore, in this paper, the degradation and stability issues associating with nanostructured energy devices will be discussed in more detail using the promising DSSCs and nanocomposite fuel cell technologies as examples. Common research methodologies for stability studies will be discussed first, followed by possible degradation mechanisms of each. Then some recent works on enhancing the stability of DSSC and SDC nanocomposite fuel cell will be presented.

2. Overview of methodologies for degradation analyses

Electronic components have traditionally been subject to standardized testing procedures to secure their durability under varying conditions. Such procedures can also be found for new energy technologies such as photovoltaic modules or solar thermal collectors. A key component in these tests is to accelerate ageing and degradation processes in controlled laboratory conditions, and to include extreme operational conditions in the tests [6]. The accelerated tests intend to cause within a reasonable time frame a cumulative stress which corresponds to that over the perceived life-time of the tested energy component. For example, degradation may be linked to chemical reactions in which case the accumulated reaction rate should correspond to the expected value over the life-time, i.e. $\sim \Sigma e^{-\Delta/kT}$, where Δ = activation energy, T = temperature.

In case of nano-energy devices the procedures for degradation analysis are not yet well established as these devices are still mainly in a research and development phase. Also, the degradation processes are not always well understood as these take place on a nano-level, but having an effect on the device performance. Therefore, we propose here a three-level degradation analysis procedure to better link and understand how degradation at nano-level and in nanostructures reflects into device performance and stability. The new procedure proposed contains nano, micro, and macro level analyses, but also highlights the manufacturing processes used in each stage (Fig. 1). The essence of the nano-level analysis is to link nanomaterials, nanostructures, morphologies and their changes to nano-energy device performance, e.g. synthesized through novel wet chemistry methods. The characterization of these nanomaterials requires in-depth advanced characterization instrumentations (HR-TEM, TEM, SEM, XRD, thermal analysis, XPS, EDX, etc.), which help to understand the structure–property relationships. In the micro-level analysis, small nanoenergy devices in laboratory-scale are fabricated from the nanomaterials through proper manufacturing methods (e.g. here with cold/hot pressing and SPS for fuel cell, doctor blading for DSSCs). The analyses will yield relevant device performance data and includes e.g. EIS, four-probe DC tests, I–V measurements, etc. in laboratory conditions. On this level, long-term *in situ* techniques allow continuous measurement during the degradation test, such as conductivity and I–V measurements; while some *ex situ* post-mortem analyses of devices, e.g. electron microscopy, can assist to detect detailed factors resulting in performance degradation or even failure. In the final stage, the macro-level, devices for real-condition use need to be fabricated by industrial scaling-up techniques for final verification of the technology. The degradation tests to be done at this level would actually merge with those used today for microelectronics and energy technology as described earlier in this section. Typically, for electrochemical nano-energy devices key macro-level tests include continuous I–V measurements in cycling conditions e.g. in weather chambers or similar.

An important aspect of the three-level procedure described above is the linkage of the degradation processes, which take place at nano-level, device performance at micro- and macro-level. The procedure helps to identify the reasons for degradation and also find ways to improve device stability. The time needed for accomplishing the necessary analyses in Fig. 1 increases from nano to macro level so that the final durability and ageing tests of full-scale devices may require several thousands of operational hours whereas the material characterization normally takes a couple of days only.

3. Degradation and stability of nanostructured DSSCs

A DSSC is a photovoltaic device which consists of a photo-electrode, counter electrode and a redox shuttle (electrolyte). These cells can be built in varying size, but also applicable for micro-electronics. A high efficient DSSC is determined by several crucial components, including panchromatic photo-absorption of dyes, rapid electron transfer at photo-anodes, good electrolytes with fast ion transportation, and efficient reduction of redox media at the counter electrodes (CEs) (see Fig. 2). The long-term stability and performance of the DSSC is currently a major concern for its further commercialization.

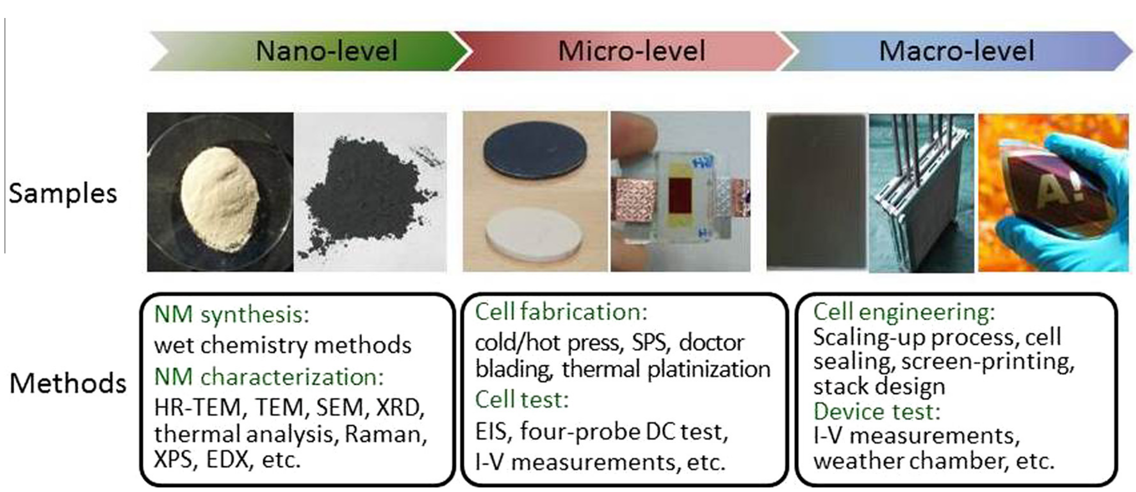

Fig. 1. Research methodologies for degradation studies of nano-energy devices (e.g. DSSC and nanocomposite fuel cell) on three different levels: nano, micro and macro level. NM: nanomaterials.