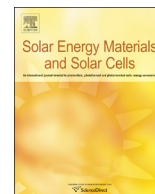




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## Size effect of synthetic saponite-clay in quasi-solid electrolyte for dye-sensitized solar cells



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### ABSTRACT

The use of a synthetic saponite-clay with different morphological features is proposed in this work as additive for DSSC solar cells electrolyte. The dilution of the synthesis gel allowed to decrease the saponite particle size from *ca.* 200 nm to *ca.* 50 nm and to obtain samples with different lamellae organization. The influence of these parameters on solar cell performances have been tested by dispersing 5 wt% of the clay in Z-946 liquid electrolyte and using the dispersion as non-liquid electrolyte. The stability of saponite dispersions in methoxypropionitrile solvent has been studied by Dynamic Light Scattering (DLS). The electrochemical characterization showed that the addition of the saponite sample with the largest particles does not influence the solar cell efficiency, whereas the use of electrolyte having saponite suspension with the smallest particle size led to an increase of solar cell efficiencies of 8% with respect to the reference cell. Finally, tests devoted to investigate the stability over the time of DSSC prepared by using quasi-solid saponite-based electrolytes have been carried out.

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### 1. Introduction

Dye-sensitized solar cells (DSSCs) are a promising technology due to their high-energy conversion efficiency under diffused light irradiation and low production cost with respect to traditional silicon-based solar cells [1]. These type of devices are inspired to photosynthesis process and the working principle is based on ultrafast electron injection from a photoexcited dye into the conduction band of a TiO<sub>2</sub> anode with subsequent dye regeneration and hole transportation to the counter electrode [2]. Up to now, conversion efficiency of new generation dye-sensitized solar cells reached 11.5% with an organic liquid-based electrolyte containing triiodide/iodide as a redox couple [3]. Nevertheless, liquid electrolytes present several technological problems such as solvent evaporation, leakage and environmental toxicity. Different solutions have been proposed to replace liquid electrolytes in DSSC devices including solid-state (*i.e.* *p*-type semiconductors [4,5]) and quasi-solid electrolytes. In particular, among materials used for the preparation of quasi-solid electrolytes, organic hole transporting materials [6,7] and solvent-free polymer electrolytes incorporating

triiodide/iodide as a redox couple [8,9] have been proposed. More recently, inorganic nanoparticles have been also taken into account and used as additives to stabilize liquid electrolytes, thus obtaining stable suspensions or gels. For instance, Graetzel et al. reported interesting results for solar cells based on a stable non-liquid electrolyte obtained by mixing amorphous silica nanoparticles and a combination of N-methyl-benzimidazole and 1-methyl-propylimidazolium iodide ionic liquids [10]. This quasi-solid-state electrolyte offered specific benefits over the ionic liquids allowing the fabrication of flexible, compact, laminated all solid-state devices free of leakage. Other research groups reported that SiO<sub>2</sub> nanoparticles have positive effects on the diffusion of redox couples in the ionic liquid based electrolyte [2]. Mesoporous silicas (*i.e.* SBA-15) and other solids (*i.e.* carbon nanotubes, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, etc.) have been also successfully used as additives to stabilize DSSC electrolytes [11–13]. More recently, both natural clays (such as laponite, montmorillonite, mica) and organo-modified layered materials (used to improve the affinity between the additive and the electrolyte) have been proposed as electrolyte gelating agents and they can be considered a valid alternative to already proposed solids. In some cases, the addition of clays to liquid electrolytes resulted in an increase of devices photocurrent density and light conversion efficiency [14–16].

Nevertheless, difficulties in the use of natural clays are often associated to the fact that the chemical composition and the physico-chemical properties of these materials (*i.e.* structure,

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particle size, morphology) are strongly variable and depend on the genesis and extraction site of the materials. In the light of these considerations, synthetic saponite clays belonging to smectite family have been prepared in this work with controlled particle size and morphology and they have been used as additives for the stabilization of liquid electrolyte.

Saponite are phyllosilicates of the 2:1 type and has a lamellar TOT structure. The general formula of the saponite is  $M_{x/n}^{n+} [Mg]_6(OH)_4[Si_{8-x}Al_x]O_{20} \cdot mH_2O$ , where  $M$  is the interlayer cation,  $x$  is the fraction of aluminum present in the structure and  $m$  is the number of water molecules [17]. Saponite clays have been largely studied in the literature due to their high specific surface area, acidity and thermal stability. In the last years, our research group deeply studied the physico-chemical properties (*i.e.* morphology, texture, structure and surface features) of synthetic saponites prepared by varying the  $H_2O/Si$  molar ratio (from 20 to 150) in the synthesis gel, which has proven to be a crucial parameter in the hydrothermal synthesis of aluminosilicates [18–20]. It was shown that the higher the dilution of the starting gel, the smaller the lamellae of the products obtained after crystallization and the higher is the specific surface area.

In this work, saponite solids with different particle size and spatial lamellae organization have been used as additives for the preparation of quasi-solid electrolytes based on triiodide/iodide redox couples and methoxypropionitrile solvent for DSSC purposes. The effect of particles size on final DSSC performances have been especially investigated. Stability over the time of devices prepared with quasi-solid electrolytes has also been evaluated in comparison to a reference DSSC cell based on standard liquid electrolyte.

## 2. Experimental section

### 2.1. Synthesis of sodium saponite samples

Synthetic saponite samples with gel composition of 1  $SiO_2$ :0.835  $MgO$ :0.056  $Al_2O_3$ :0.056  $Na_2O$ : $xH_2O$  ( $x=20, 110$  and  $150$ ) and nominal cationic exchange capacity (CEC) of 104.9 meq/100 g were prepared by modifying the literature method indicated by Kloprogge et al. [21]. The amorphous silica (11.9 g,  $SiO_2$  99.8%, Aldrich 381268-500G, M.W.=60.09) was dispersed in a solution prepared by dissolving 0.92 g of NaOH (Carlo Erba, 1310-73-124 2, M.W.=39.997) in a part of needed water. The obtained gel was mixed with a Teflon rod and a mechanical stirrer. After 1 h, magnesium acetate tetrahydrate (35.8 g  $Mg(CH_3COO)_2 \times 4 H_2O$  99%, Aldrich 22,864-8, M.W.=214.455) and aluminum isopropoxide (4.7 g  $Al [OCH(CH_3)_2]_3$  98+%, Aldrich 22,041-8, M.W.=204.25) were added to the gel, along with the remaining water. After 2 h, the gel (with pH about 8–9) was introduced in a Teflon cup (125 mL capacity) of an autoclave (Anton PAAR 4748) and heated in an oven at 513 K for 72 h.

Different saponite samples were prepared by varying the  $H_2O/Si$  molar ratio in the synthesis gel. In particular,  $H_2O/Si$  molar ratio of 20, 110 and 150 were used. Samples will be named SAP $x$ , where  $x$  is the  $H_2O/Si$  molar ratio used for the synthesis gel preparation (SAP20, SAP110 and SAP150).

After the hydrothermal treatment, samples were filtered, washed with 2 L of deionized water and dried in an oven for 36 h at 393 K. SAP $x$  materials were submitted to a classical ion exchange procedure in a saturated NaCl solution for 36 h at room temperature (*rt*) to replace cations that beside  $Na^+$  ions, can be present in the interlayer space such as  $Al^{3+}$  and  $Mg^{2+}$ . Then, the solids (hereafter named NaSAP $x$ ) were filtered and washed with deionized water until the complete elimination of the chloride that was tested by  $AgNO_3$  solution.

### 2.2. Cell assembly

A 12  $\mu m$  thick  $TiO_2$  film (18 nm particle size, Ti-Nanoxide T/SP, Solaronix) was screen-printed on a fluorine-doped tin oxide conducting glass electrode (7  $\Omega/cm^2$ , TCO22-7, Solaronix) and used as photoelectrode. After the sintering at 773 K, the  $TiO_2$  electrodes were dye-coated by immersing them into a 0.5 mM solution of cis-diisothiocyanato-bis[2,2'-bipyridyl-4,4'-dicarboxylato] ruthenium[II] bis[tetrabutylammonium] dye (N719, Ruthenizer 535-bisTBA, Solaronix) and 5.0 mM of staining additive chenodeoxycholic acid (Solaronix) in methanol ( $CH_3OH$  99.8% Aldrich) at room temperature for 16 h. Counter electrodes were prepared by applying a drop of platinum precursor (Platisol T, Solaronix) on a fluorine-doped tin oxide glass, followed by sintering at 748 K for 25 min. The electrodes were separated by 60  $\mu m$ -thick hot melt polymer (Meltonix 1170-60 PF, Solaronix) and sealed up by heating.

Non transparent cells were prepared by screen-printing *ca.* 3–4  $\mu m$  of  $TiO_2$  with particle size over 100 nm (Ti-Nanoxide R/SP, Solaronix) on top of the previously prepared 12  $\mu m$  transparent electrodes.

The active area of the prepared devices was 0.36  $cm^2$  and for accurate measurement a black mask was used during photovoltaic characterization.

The DSSC devices were submitted to accelerated aging test for 1200 h in a solar simulator with a light intensity of 100  $mW/cm^2$  (full sun, AM 1.5 G) at 333 K and ambient relative humidity, following the ISOS-L-2 protocol [22]. The cells were subjected to a perpendicular light beam exposition with constant and uniform irradiation over their entire surface. Before exposition, all devices were secondary sealed with epoxy glue and covered with a UV cutoff filter (up to 400 nm).

### 2.3. Quasi-solid electrolyte preparation

Quasi-solid electrolytes were prepared by dispersing the NaSAP $x$  samples (5 wt%) in 3-methoxypropionitrile based electrolyte (Z-946). Dispersions were stirred for 16 h at room temperature. The electrolyte-injecting hole was made with a drill on the counter-electrode glass substrate and the electrolyte suspensions were injected in the cells under vacuum.

### 2.4. Instruments and measurements

- Chemical composition of saponite samples was determined by inductively couple plasma-mass (ICP-MS) and atomic adsorption spectroscopy (AAS) by ITECON laboratory (Nizza Monferrato, Italy).
- X-ray diffractograms (XRD) were collected on unoriented ground powders with a Thermo ARL XTRA-048 diffractometer with a  $Cu K_{\alpha}$  ( $\lambda=1.54 \text{ \AA}$ ) radiation. Diffractograms were recorded at *rt* between 2 and 65°  $2\theta$  degrees with a step size of 0.02°  $2\theta$  and a rate of 1°  $2\theta/min$ .
- TEM images were collected on a JEOL 2010 High Resolution Transmission Electron Microscope operating at 300 kV. Specimens were prepared by sonicating the sample in isopropanol and by depositing a drop of the suspension on carbon-coated grids.
- The particles size analysis was performed by photocorrelation spectroscopy with a Zetasizer NANO ZS (Malvern Instruments). Before the analysis the samples were dispersed (5 wt%) in 3-methoxypropionitrile and stirred for 16 h at room temperature.
- Photocurrent density–voltage curves characterization was carried out at 1.5 AM illumination using a Keithley 2400 source measure unit. A 1000 W halogen lamp (SolarSim-150, Solaronix) served as light source and its intensity was adjusted with a Si reference (IXYS XOB 17-04  $\times 3$ ) for 1 sunlight intensity of 100  $mW/cm^2$ .

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