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Low temperature sintering of aqueous TiO₂ colloids for flexible, co-sensitized dye-sensitized solar cells



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ABSTRACT

Colloidal TiO₂ films have been prepared using a binder-free aqueous paste with Degussa P25 and hexafluorotitanic acid (H₂TiF₆), which was optimised for different substrates. Dye-sensitized solar cells (DSSC) fabricated using this paste were sintered at (*ca.* 393 K) and efficiencies (η) of 3.0, 4.2 and 6.1% were measured for devices using titanium foil (*ca.* 1 mm thickness), indium-doped tin oxide on polyethylene terephthalate (ITO-PET), and for co-sensitized devices on fluorine-doped tin oxide (FTO) glass substrates, respectively. Electrochemical impedance measurements show that the charge transport resistance is less consistent for devices fabricated at low sintering temperature (*ca.* 393 K) by comparison to devices sintered at 773 K. These measurements correlate with the increased variation in device efficiency (η) for low temperature sintered DSSC devices.

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1. Introduction

DSSCs have been reported with efficiencies of *ca.* 13 [1] and 14% [2] for verified and un-verified measurements. It was reported that these devices were fabricated using high temperature (*ca.* 773 K) sintering of the TiO₂ photoanode to ensure optimised interparticle connectivity. Fabrication of DSSCs using photoanodes sintered at low temperature is desirable for large scale commercialisation since this will decrease the financial/ energy processing costs and broaden the range of substrates available. The first report of low temperature sintering of DSSC photoanodes (*ca.* 573 K) made from organic-binder containing pastes was achieved using peroxide combustion giving $\eta = 7.5\%$ [3]. However, this temperature is still too high for plastic substrates which require sintering <400 K. So, for low temperature sintering on plastic substrates, the highest η reported is 8.1% using compression methods [4] although, recently $\eta = 8.75\%$ was reported using hybrid dye-titania nanoparticles on FTO-glass sintered at <473 K making this the highest η for low temperature sintered DSSC devices reported to date [5].

In terms of low temperature chemical sintering, Pasquier *et al.* reported η of 5% at 0.5 sun for TiO₂ photoelectrodes on ITO-polyethylene naphthalate (ITO-PEN) sintered at 423 K using hexafluorosilicic acid as a binding agent [6] and Miyasaka *et al.* reported η of 5.8% for mesoscopic TiO₂ films sintered at 383–398 K on ITO-PEN using HCl [7]. In this work, we report the low temperature sintering of a binder-free TiO₂ paste using H₂TiF₆ as

a novel chemical sintering agent along with co-sensitisation using N719 and SQ1 dyes to achieve amongst the highest η reported for binder-free pastes without additional compression treatment.

2. Experimental

Three conducting substrates were used; ITO-PET (15 $\Omega \square^{-1}$, Optical Filters), FTO-coated glass (TEC15, 15 $\Omega \square^{-1}$, NSG) or titanium foil (>99.6%, 1 mm, Advent Research Materials). All substrates were rinsed with de-ionised water and isopropanol before use. Titania pastes were prepared by adding various volumes of hexafluorotitanic acid (60% H₂TiF_{6(aq)}, Aldrich) to a stirring suspension of P25 (1 g, Degussa) in 4 ml de-ionised water. Upon addition of the acid the suspension forms a viscous paste which was left to stir for 5 min before use. Photoanodes (*ca.* 1.0 cm²) were prepared by doctor blading TiO₂ pastes onto each of the conducting substrates using 1 layer of Scotch™ (3 M) tape as a spacer. Films were sintered by heating at 10 K min⁻¹ in an ashing furnace either at low (dwell at 393 K) or high temperature (dwell at 773 K). Films were then immersed in 50 mM TiCl₄:THF_{2(aq)} at 343 K for 30 min, rinsed with de-ionised water, air-dried for 10 min before re-sintering at the same temperature as the initial sinter for 30 min. Sensitisation using N719 and SQ1 dyes was as reported in [8]; full details are in electronic [supplementary information \(ESI-1\)](#).

3. Results and discussion

H₂TiF₆ was used as a binding agent to chemically sinter the TiO₂ particles together and to the substrate. Because this aqueous paste

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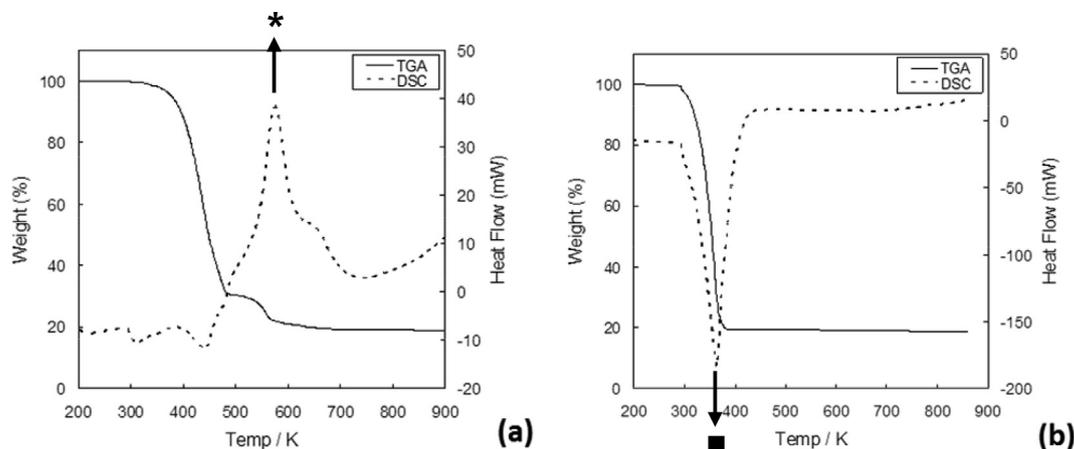


Fig. 1. TGA-DSC data for (a) P25 TiO_2 paste containing ethyl cellulose and terpineol solvent showing exotherm (*) for organic combustion at ca. 600 K and (b) aqueous P25 paste containing H_2TiF_6 showing endotherm (■) for H_2O evaporation at 373 K.

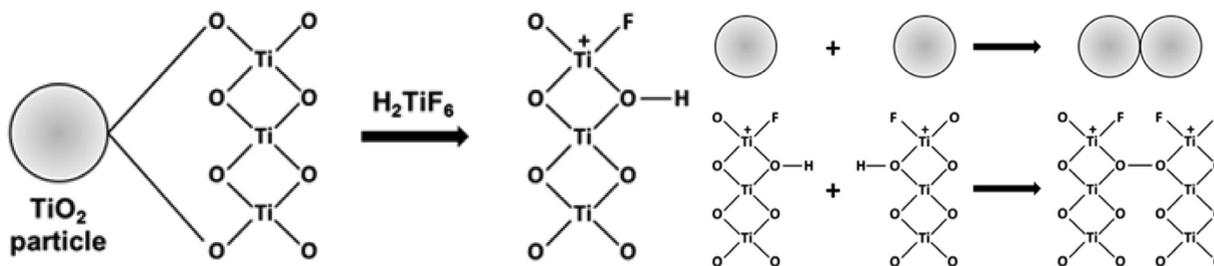


Fig. 2. Schematic of the "etch-deposition" process of H_2TiF_6 which shows the action of F^- on the surface of TiO_2 particles (left) followed by a condensation reaction between two TiO_2 particles (i.e. chemical sintering – right) which promotes TiO_2 to TiO_2 and TiO_2 -substrate adhesion.

does not contain organic polymers to control paste rheology the combustion of organics at temperatures above 473 K is not required as is shown in the thermogravimetric analysis-differential scanning calorimetry – TGA-DSC data (Fig. 1).

Instead of a high temperature, heat-driven process at 773 K, interparticle connectivity occurs because of a condensation protonation-dehydration reaction (Fig. 2) on the surface of the TiO_2 whilst the by-product of H_2TiF_6 hydrolysis is more TiO_2 . The Sn–O–Ti bonds formed between ITO and TiO_2 form due to a similar reaction.

Pasquier et al. reported chemical sintering using hexafluoroarsinic acid (H_2SiF_6) [6]. However, one advantage of H_2TiF_6 over H_2SiF_6 is that it will leave TiO_2 as a hydrolysis by-product instead of SiO_2 . In addition, less H_2TiF_6 is required to prepare optimised photoelectrodes (10–75 μl of 60% $\text{H}_2\text{TiF}_6(\text{aq})$) by comparison to the 125–500 μl of 20% H_2SiF_6 reported in [6]. Pasquier et al. also reported that the same quantity of acid was used to prepare optimised photoelectrodes on both FTO-glass and ITO-PEN [6]. Our data show that the optimum quantity of H_2TiF_6 varies depending on the substrate used (Table 1). Thus, excess H_2TiF_6 reduces device η by lowering fill factor and photocurrent for devices fabricated on ITO-PET and FTO-glass. This reflects over-etching of the TiO_2 surface and underlying ITO or FTO conducting layers and was also reported for the H_2SiF_6 devices where electrochemical impedance spectroscopy (EIS) showed that excess H_2SiF_6 addition caused over etching of the ITO coating and a loss in conductivity of the substrate [6].

Interestingly, devices fabricated on Ti foil using 50 or 75 μl of H_2TiF_6 show an increase of photocurrent (Table 1). This is due to the substrate conductivity being less sensitive to acid etching; i.e. the Ti foil is a conductor and does not rely on a layer of conducting oxide on the surface as is required for FTO-glass or ITO-PET. The open circuit voltage (V_{oc}) decreased with increasing acid quantity

Table 1

Current voltage (I–V) data for dye-sensitized solar cell devices made using varying quantities of $\text{H}_2\text{TiF}_6(\text{aq})$ in aqueous pastes sintered at 393 K. η = power conversion efficiency; FF = fill factor; J_{sc} = short circuit current; V_{oc} = open circuit voltage. †Device measured under reverse illumination ‡Control device sintered at 773 K †Devices sintered at 393 K but co-sensitized with N719 + SQ1 dyes.

Substrate	$\text{H}_2\text{TiF}_6/\mu\text{l}$	$\eta/\%$	FF	$J_{sc}/\text{mA cm}^{-2}$	V_{oc}/V
ITO-PET	10	2.9	0.66	5.3	0.84
	15	4.2	0.71	7.2	0.83
	20	3.2	0.68	5.5	0.86
FTO-glass	30	3.8	0.64	7.6	0.78
	35	4.5	0.69	8.5	0.77
	40	4.1	0.68	8.0	0.76
Ti foil†	30	2.2	0.66	4.9	0.70
	50	3.0	0.66	6.9	0.76
	75	2.8	0.64	7.1	0.61
FTO‡	35	5.5	0.63	11.4	0.76
FTO†	35	6.1	0.66	11.0	0.83

for FTO and Ti foil devices. However, ITO-PET based devices show increased V_{oc} when more H_2TiF_6 is used. For the control devices (sintered at 773 K on FTO-glass), η is 5.5% versus $\eta = 4.5\%$ for 393 K sintering due to increased photocurrent (11.4 versus 8.5 mA cm^{-2} , respectively). We also report what we believe is the first co-sensitisation of low temperature sintered photoelectrodes which increases J_{sc} to 11.0 mA cm^{-2} and V_{oc} by 0.10 V to 0.86 V; resulting in an overall η of 6.1%.

Electrochemical impedance spectroscopy (EIS) is a useful method for separating the impedance contributions of processes at electrode interfaces in DSSC devices. DSSC Nyquist diagrams typically show 3 semi-circles with increasing frequency for Nernst diffusion within the electrolyte due to electron transfer at the oxide/electrolyte interface and the redox reaction at the Pt

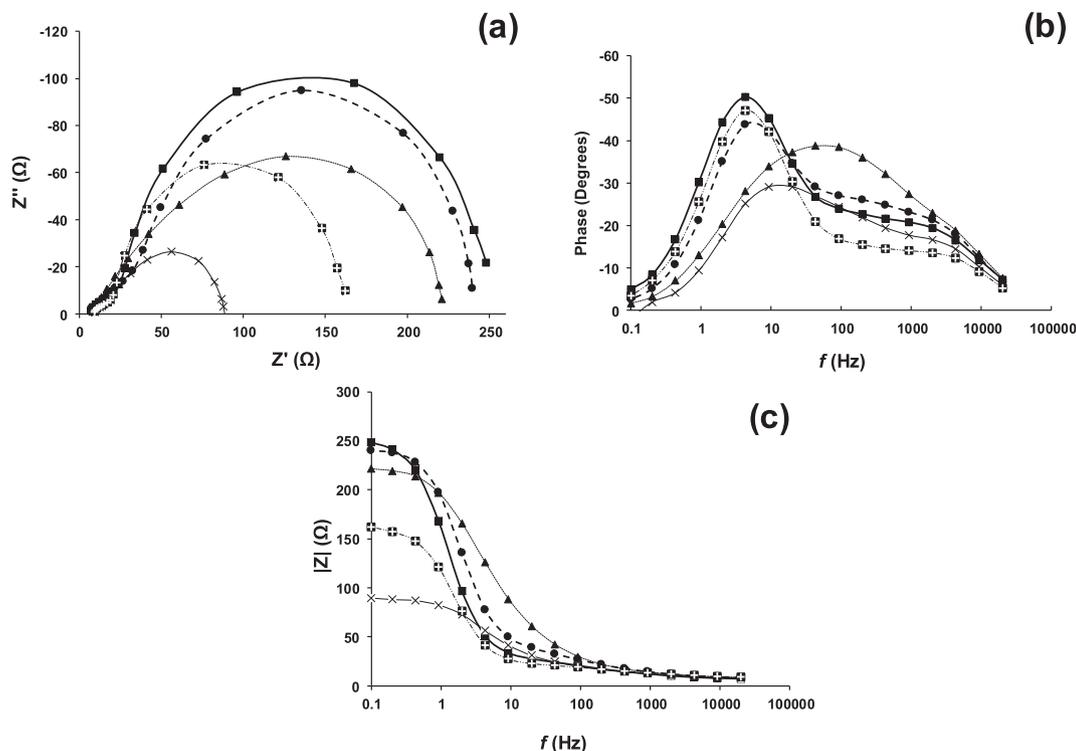


Fig. 3. (a) Nyquist plots (b) Bode phase plots and (c) Bode magnitude data of the electrochemical impedance spectra for devices prepared using replicate electrodes sintered at 773 K (black squares and circles) or 393 K (black triangles, black crosses or white crosses on black squares).

counter-electrode [9]. The EIS data shown in Fig. 3 can be correlated with the IV data summarised in ESI Tables 6 and 7 [ESI-4] which show device data for DSSCs fabricated on FTO-glass with 35 μl H_2TiF_6 and sintered at 393 K or 773 K. Whilst the overall η measured for both high and low temperature sintered devices was similar, the Nyquist plots (Fig. 3a) show a wider variation for the electrodes prepared at 393 K and lower impedance values for (Z' Ω). This means that the charge transport resistance for TiO_2 electrodes sintered at 393 K was inconsistent compared to devices prepared at 773 K. A higher overall Bode phase shift (Fig. 3b) and Bode phase magnitude (Fig. 3c) was measured at a slightly lower frequency for devices sintered at 773 K. This could be due to improved interparticle connectivity resulting in increased electron lifetime in the photoanode.

4. Conclusions

These data show that H_2TiF_6 can be used as a chemical sintering agent to fabricate TiO_2 photoanodes at low temperature (393 K) on ITO-PET, FTO-glass or Ti foil. The data also clearly show that there is an optimum H_2TiF_6 concentration which is strongly dependent on the substrate used and which increases from ITO-PET to FTO-glass to Ti foil. This optimum is related to the etch-deposition action of H_2TiF_6 whereby too much of the acid over-etches the substrate reducing fill factor and photocurrent. EIS data show that the wider variation of η for 393 K sintered DSSC devices is due to increased charge transport resistance in the photoanode compared to 773 K sintered devices. We also report what we believe to be the first co-sensitized low temperature fabricated DSSC device giving $\eta = 6.1\%$ for a N719/SQ1 dye combination.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2018.10.118>.

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