# Nanoporous zeolite film electrodes†

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**Nanoporous and oriented zeolite A films have been synthesized on tin oxide substrates. The films can be modified to reject or pass molecular oxygen to an underlying electrode; films such as these show great promise for template-assisted growth of nanostructures.**

The motivation for placing zeolite thin films on conducting and semiconducting substrates stems from a desire to control the route that gas and solution phase species take to the gas/solid or gas/liquid/solid interface. Since the early 1990s several reports on the growth of zeolitic films have appeared,[1,2] the majority on non-conductive substrates such as glass or quartz. Most were not oriented or coherent (*i.e.*, fully covered the substrate). This communication deals with zeolite films directly synthesized on electrodes using sol–gel methodology. The principal advantage of this approach is that oriented films can be grown. Jansen *et al.*[3] and Mintova *et al.*[4] have both reported oriented films on conductive substrates. Although these films were apparently continuous there was little discussion of the quality of the films in terms of their mesoporosity. Unless careful size exclusion measurements are undertaken (*vide infra*) it is impossible to estimate the number and size of defects in the film, and how these may effect its transport properties. Below we discuss the first example of an oriented and coherent zeolite film on a planar conductive electrode where the film behaves as a nanoporous filter in an electrochemical environment. In addition, we show that electrochemical methods can be used to assess the quality of the film in terms of its molecular sieving properties.

Zeolite films were generated using methods based on the seed and feed approach developed by Hedlund *et al.*[5] In our laboratories, colloidal zeolite seed crystals are adsorbed onto charge reversed tin oxide surfaces followed by hydrothermal crystallization of the zeolite film using a sol feedstock. Tin oxide surfaces were charge reversed by adsorption of a cationic polymer (Eka ATC 4050, Eka Chemicals, Marietta, Georgia, USA) and allowed to dry. Seed crystals were synthesized using the methods described by Schoeman *et al.*.[6] 125 µL of an aqueous suspension of the colloidal seed crystals was then applied to the tin oxide surface and air-dried. Following this the electrodes were immersed in a feedstock gel with molar composition $Al_2O_3 : 4.78 Na_2O : 10.5 SiO_2 : 190 H_2O$, and heated within a closed polypropylene bottle at 100 C for 5 h. This feedstock produced sodium zeolite A. Superior films were produced when the electrodes were positioned face down during the syntheses. Electrochemical measurements were effected using a PAR 273A potentiostat. Chronocoulometry was performed by applying a potential step from the open-circuit potential. Measurements at unmodified and coated tin oxide electrodes were made sequentially in the same cell without breaking the oxygen purge in order to ensure that the concentration of oxygen was the same in all experiments.

The XRD of a Na zeolite A film grown in this manner is shown in Fig. 1. Compared to the diffraction patten of the bulk material it is clear that the zeolite film is highly oriented by
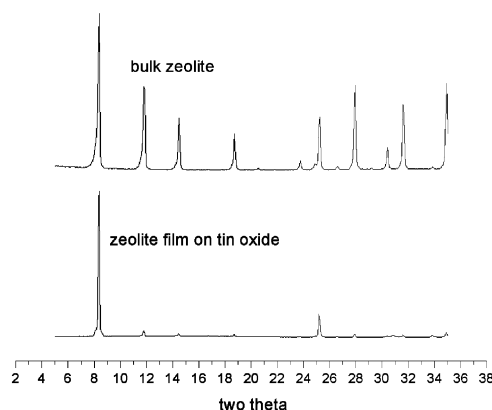


**Fig. 1** XRD of sodium zeolite A film on tin oxide compared to a bulk powder.

virtue of the large intensity of the {200} reflection ($2\theta \approx 8°$ of the cubic zeolite A unit cell.

Cyclic voltammograms of these films in water are shown below. The films behave differently depending on the nature of the zeolite extraframework cation. In the figure, reduction of molecular oxygen is apparent at ca. −1.5V at bare tin oxide and tin oxide covered with sodium zeolite A (NaA). However, when the electrode is coated with potassium A (KA) reduction of oxygen is suppressed. Note that ion exchange of sodium for potassium was effected *in situ*. XRD analysis showed no change in crystallinity or orientation of the films.

This is a reflection of the distinct pore sizes of the two zeolites. KA possesses a 3 Å pore (commonly called 3A zeolite) *cf.* that of NaA which is 4 Å. Molecular oxygen with a diameter of 3.145 Å is rejected by the KA film and cannot reach the electrode surface. This indicates that these *oriented* films show nanoporosity in an electrochemical environment. Moreover, the diffusion of oxygen through defects in the films is apparently of
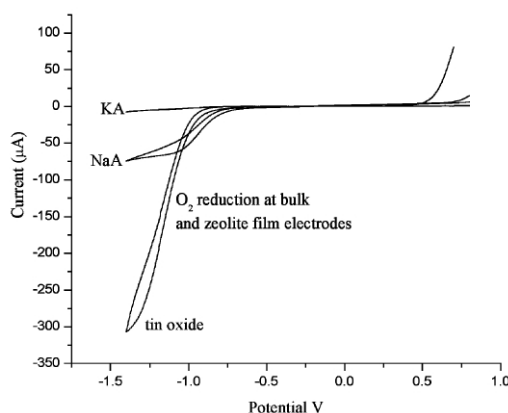


**Fig. 2** Cyclic voltammetry of sodium zeolite A films in water. Oxygen reduction is suppressed with KA due to pore size restrictions. Supporting electrolyte: 0.1 M NaNO₃ (NaA and tin oxide), KNO₃ (KA). Scan rate: 20 mV s⁻¹. Electrodes were immersed in solution following 30 min oxygen purge prior to voltammetric measurements.

† Electronic supplementary information (ESI) available: Fig. S1: SEM of non-oriented sodium zeolite A film, Fig. S2: SEM close up of oriented zeolite A film. See http://www.rsc.org/suppdata/cc/b2/b204042e/
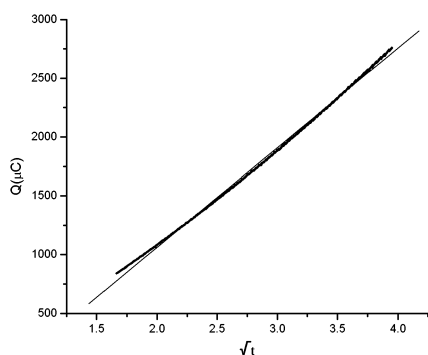
**Fig. 3** Chronocoulometry at an unmodified tin oxide electrode. Electrolyte: $NaNO_3$ saturated with oxygen. Potential step $-1.25$ V.
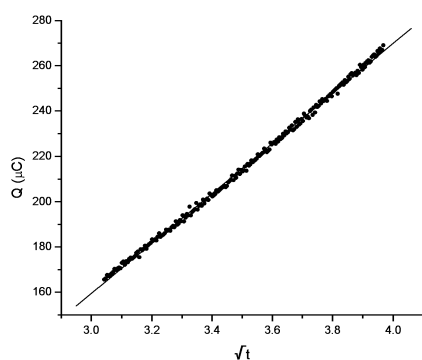


**Fig. 4** Chronocoulmetry at tin oxide electrode coated with a NaA film. Electrolyte: 0.1 M $NaNO_3$ saturated with oxygen. Potential step $-1.25$ V.

minor importance. The films thus consist of a nanoporous and organized array of zeolites on the electrode surface. Note that one cannot merely use the ratio of the reduction currents at KA and NaA films to assess the proportion of defects. One must first ascertain the diffusion coefficient of oxygen in zeolite A.

In Fig. 3 we show chronocoulometry for oxygen reduction at a bare tin oxide electrode and in Fig. 4 the data collected at a NaA film. In both cases the data follow the Cottrell equation ($i = nFA(D/\pi)^{1/2}Ct^{-1/2}$). The diffusion coefficient of oxygen can be determined from this data *via* a comparison of the relative slopes. The diffusion coefficient of oxygen in water is reported to be[7] $2.26 \times 10^{-5}$ cm$^2$ s$^{-1}$ whereas in zeolite 4A Sun and Costa[8] have reported a value of $3.5 \times 10^{-7}$ cm$^2$ s$^{-1}$. In good agreement with this, the data in Fig. 3 and 4 lead to a value of $3.7 \times 10^{-7}$ cm$^2$ s$^{-1}$. This lends further credence to the interpretation of the data shown in Fig. 2. That is: molecular oxygen reaches the electrode *via* the zeolite pore system and not *via* defects and/or grain boundaries. Oriented and defect-free films such as these have great promise for template-assisted electrodeposition of nanostructures, since nucleation and
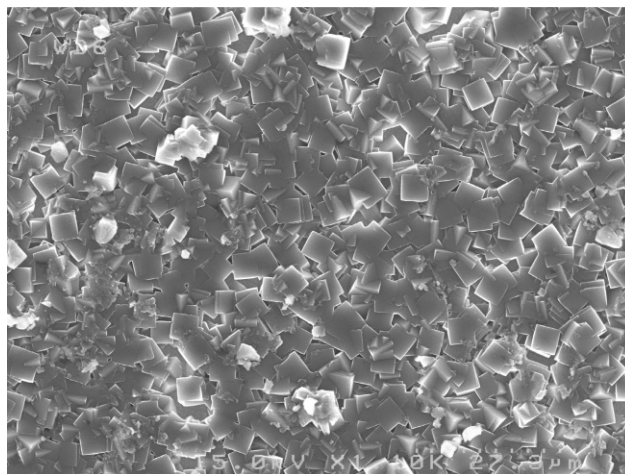


**Fig. 5** Scanning electron micrograph of sodium zeolite A film on tin oxide. Accelerating voltage 15 kV, emission current 10μA.

growth of metals, semiconductors and polymers at the electrode surface can in principle be constrained by the zeolite pore system. This will not require perfect registry of the film at the substrate. Further study of electrodeposits at these and other oriented and coherent zeolitic films will be required.

In Fig. 5 we show a typical SEM of a sodium zeolite A film. The square faces of the oriented cubic zeolite crystals are clearly observable. There is also some disorder. The relative ordering of the individual zeolite crystals will be further studied *via* an XRD texture analysis. Film thickness ranged between 500 nm and 2 μm.

## Notes and references

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