Notes

A Fast Way to Make a Monolithic Column for a High Pressure Electroosmotic Pump

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A simple way was proposed to make a monolithic column for a high pressure electroosmotic pump (EOP). It is *in-situ* synthesized inside the silica capillary from potassium silicate solution and no frit is required. Compared with common approaches to make columns for EOP, the present method is robust and fast (<4 h). For pure water, a stand-alone EOP operated at 15 kV applied voltage is capable of generating a flow rate of 3.1 μL/min and a maximum static pressure of ~5.4 MPa.

Introduction

Electroosmotic pumps (EOP) have attracted much interest recently due to some attractive features.[1] EOPs require no moving parts and are easily fabricated. In addition, precise flow rate or flow direction control can be achieved with a simple current or voltage-control circuit that is particularly well suited for miniaturized systems.

The conduit in which the electroosmotic flow is produced is the key component of EOPs. Open channel (commonly a segment of open silica capillary)-based EOPs are simple to be fabricated; its drawback is poor pressure output capability. Thus it is always applied for flow injection analysis (FIA).[2,3] The packed configurations are capable of generating higher pressure output. The capillary columns packed by silica packings can serve as EOP conduits.[4] Frits are always required to retain the silica beads for packed columns. *In-situ* reproducible preparation of the frit is often difficult. In addition, special instruments are needed to complete the packing successfully. The use of monolithic column provides a good alternative for fabricating EOPs in view of the fact that frits are not required.[5,6] The common methods to make monolithic columns are always tedious. Commonly, at least 24 h is needed for the whole process. It would be desirable to find a fast way to make columns for fabricating EOP. Based on the method presented by Fields,[7] which was for liquid chromatography and whose whole process was lengthy (at least 30 h), here we propose a fast way to make a silica monolithic column for EOP.

Experimental

Preparation of the silica xerogel column

Briefly, the fused silica capillary (0.25 mm i.d. × 0.365 mm o.d.) was rinsed with acetone and water by a syringe. It was

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then treated with 1.0 M NaOH, washed with water, then with 0.2 M HCl and finally with water again. Next, 10 wt% of formamide was added in potassium silicate solution (Kasil No. 2130, PQ Corp., USA) and vortexed until the formamide was completely dispersed. The capillary was filled with the solution and then both ends of the capillary were sealed with silicone septa. The capillary was placed for 1 h in a column oven set at 100°C. The column was then washed with water, and methanol for 0.5 h each to remove all unreacted components, and washed with water again for 0.5 h prior to use. The whole process takes less than 4 h.

Fabrication of EOP

The EOP fabrication procedure was similar to that previously described.[8] Briefly, a xerogel column served as the EOP conduit. A platinum wire as the +HV electrode was immersed into the water vial. The end of the column was immersed in the water, and the other end was affixed in one arm of a PEEK microTee. The pump output tube was affixed to the opposing arm. The vertical arm was for placing the ground electrode. Milli-Q pure water was used unless otherwise stated. A high voltage power supply (Lion HV, Tianjin, China) was used for powering EOP. The output pressure was measured *via* a pressure sensor (SP70-A3000, Senso-Metrics, Simi Valley, USA). Flow rates were measured gravimetrically.

Results and Discussion

The effect of formamide content in the range of 6 – 12 wt% was investigated, as shown in Fig. 1. With formamide content >11%, the gel precondensation process was found to be very fast; the solution became viscous rapidly and it was difficult to introduce the capillary. With formamide contents <10 wt%, it was relatively easy to get a homogenous solution which allowed the capillary to be readily introduced. At lower formamide content, however, both electrical resistance and the electroosmotic flow produced decreased. A low electric resistance results in higher current and thus leads to higher Joule
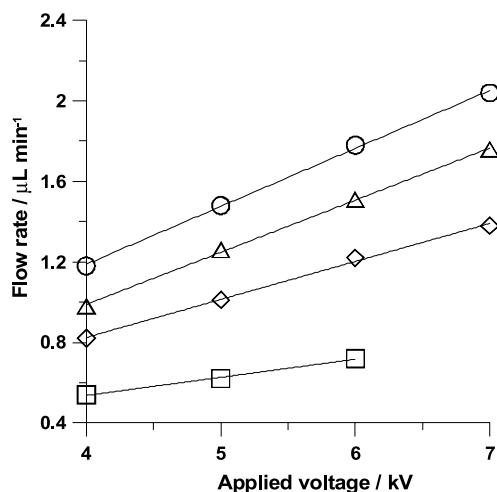
Fig. 1   Effect of formamide content on the xerogel column-based EOP.   The columns, 0.25 mm i.d. × 16 cm; pumping media, pure water. Formamide content: ○, 11; △, 10; ◇, 9; □, 7.2%.
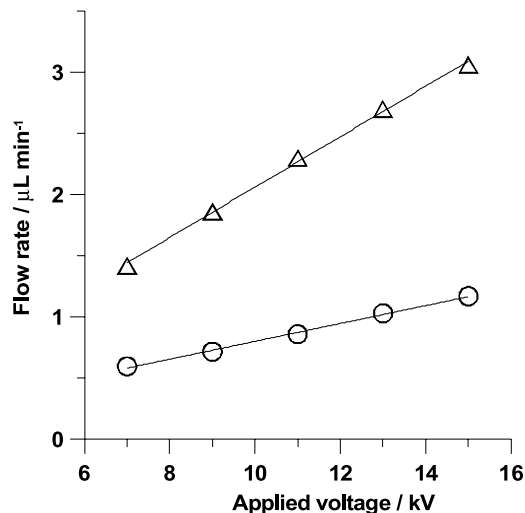

Fig. 2   Effect of applied voltage on the flow rate generated by EOP.   EOP column, 0.25 mm i.d. × 0.365 mm μm o.d. × 30 cm; ○, H_2O–methanol (1:1), $F = 0.206V + 0.002$, $R^2 = 0.9982$; △, H_2O, $F = 0.073V + 0.072$, $R^2 = 0.9969$.

heating. If the content was reduced to be <6%, the gelation process was very slow. Although the EOP prepared with 11 wt% formamide gave the highest electroosmotic flow, the high viscosity of the precursor made introduction of the capillary difficult and the columns could not be prepared reproducibly. Further experiments were carried out by 10 wt%. The column-to-column reproducibility of four columns prepared was 12% in the term of backpressure. Although the reproducibility was not so good, its fast feature obviates this drawback to a great degree.

An EOP conduit with higher hydrodynamic resistance would be desirable since it would have higher ability to resist hydrodynamic flow in the reverse direction. High hydrodynamic resistance of EOP could always be realized by increasing the packing density of the column. Based on the method presented by Gusev et al.,[9] the total porosity of the xerogel column was roughly estimated to be ~0.68. A desirable feature of the xerogel column is that it is fritless and the xerogel matrix is directly attached to the capillary wall. As a test of this, pure water was flowed through the column driven by a NanoLC pump (MicroTech Corp., USA) and the backpressure was measured as a function of flow rate. In the tested range of 0 – 4 μL/min, the pressure drop of the column was linearly related with the flow rate with the correlation coefficient of 0.9999, indicating the column had a good mechanical stability. In addition, the column showed good lifetime and could work well for at least half a year.

A highly linear relationship ($r^2 = 0.9973$) between the applied voltage and the current was observed in the tested range of 0 – 15 kV. The applied voltage and the generated flow rate also exhibited a good linear relationship, as shown in Fig. 2. The maximum flow rate generated without load was 3.1 and 1.2 μL/min for pure water and methanol/water, respectively. The maximum attainable static pressure was found to be highly linear with the applied voltage ($r^2 = 0.9999$) and the measured maximal static pressure was ~5.4 MPa. Compared to the similar EOPs reported previously, the EOP fabricated here shows good performance by considering flow rate and produced pressure, e.g. 2.9 μL/min and pressures of 0.3 MPa provided by Wang et al.,[6] 0.01 μL/min and pressure of 2.5 MPa by Paul et al.[4]

Good operational stability of EOP is a key factor to practical

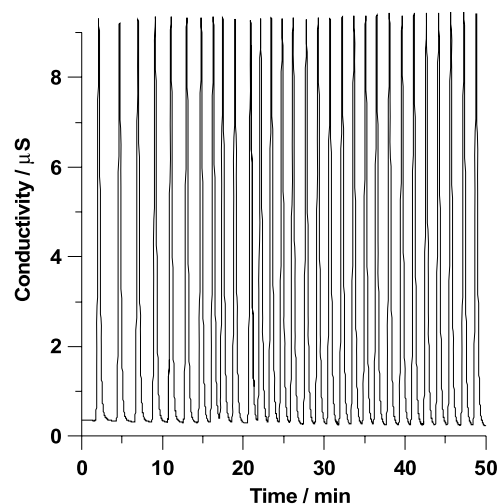Fig. 3   Thirty consecutive injections of KCl under the mode of FIA. EOP column, 0.25 mm i.d. × 0.365 mm μm o.d. × 30 cm operated at 7 kV applied voltage; pumping media, pure water; sample, 2.5 mM KCl; injection volume, 200 nL; conductivity detector, Dionex CDM-1.

application. Figure 3 shows the reproducibility of 30 consecutive injections of KCl sample in ~50 min. RSD of peak height and peak area were 0.66 and 1.47%, respectively, indicating good stability of the flow rate generated. In addition, the standard deviation of the measured flow rate in three days was 6.6%, indicating good day-to-day reproducibility. The utility of EOP is also demonstrated to couple with a KOH micro electrodialytic eluent generator (μ-EDG), which could online change pure water into KOH, a typical eluent used in ion chromatography. The produced KOH concentration is highly correlated with the applied current, as shown in Fig. 4. This indicated the practical merit of the combination of EOP-μ-EDG for capillary IC.

In summary, a fast way to make silica xerogel column for EOP was proposed. No frit and no special devices are needed for preparing the columns.
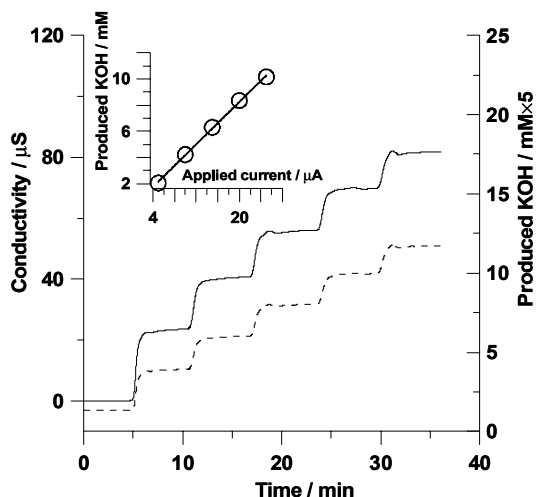
Fig. 4 Profile of conductivity and the produced KOH generated with the change of applied current of μ-EDG. Pure water flows though a μ-EDG driven by EOP, and the effluent of the μ-EDG was monitored by a conductivity detector. The applied current for each step from low to upper is 5, 10, 15, 20 and 25 μA. Solid line and dashed line are for left and right y-axis, respectively. The other conditions are as in Fig. 3.

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