

IMECE2003-44401

HIGH-PRESSURE MICROHYDRAULIC ACTUATOR

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ABSTRACT

Actuation forces of 2.1 and 5.3 pounds (9.3 and 24 N) at velocities of 1 and 0.5 mm/s have been demonstrated with compact electrokinetic pumps producing 200 $\mu\text{L}/\text{min}$ at 400 psi (2.8 MPa) and 100 $\mu\text{L}/\text{min}$ at 1000 psi (6.9 MPa). This output compares favorably with electromechanical actuators (solenoid, piezoelectric, stepper motor) of similar size and is achieved silently and with no moving parts. Electrokinetic pump monoliths based on phase-separated porous methacrylate polymer monoliths and slurry-packed, sintered silica monoliths have been developed that can generate electrokinetic pressures of 3 psi/V (21 kPa/V) and 8 psi/V (6.9 kPa/V), respectively. Corresponding maximum power conversion efficiencies of 1% and 3% have been demonstrated in 10 mM TRIS-HCl at pH 8.5. Gas-bubble-free electrodes have been demonstrated to deliver 2 mA and seal to 1200 psi (8.3 MPa) for microhydraulic actuation.

INTRODUCTION

Hydraulic work from an electrokinetic (EK) pump may be obtained, for example, by pressure-driven flow against a capillary restriction, driving a piston load, or expanding a bellows. EK pumps have a linear pressure-flowrate response due to superposition of electroosmotic and pressure-driven flows (ignoring property changes due to viscous heating or electrolyte composition). Because hydraulic power is the product of pressure and flowrate, the most efficient load condition for a given electric field is half the maximum pressure and half the maximum flowrate [1]. The

maximum power output increases linearly with electric field up to the point where changes in electrolyte or surface chemistry occur.

An important attribute of high-performance EK pump materials is a narrow pore size distribution with a mean of approximately twice the double layer thickness [2, 3], which is governed by the particular electrolyte and material combination. Pores that are too small conduct current without dragging appreciable volumes of liquid (insufficient flowrate per current), while pores that are too large do not provide sufficient pressure-driven flow resistance (excessive permeability). Millimeter-scale porous monoliths have been developed with 200-300 nanometer pores in both polymer and glass. The polymer monolith is based on the porous polymer formulations developed at Sandia [4]. The glass monolith is based on sintering of slurry-packed silica beads [5, 6]. Slurry packing has been investigated previously at Sandia [3, 7].

EK pumps are rather inefficient (1-3% typical for our pumps, 6% maximum [2, 8]) and draw substantial current densities when large electric fields are applied (100 mA/cm² at 1000 V/cm). For capillary EK pumps with 100- μm diameter, the currents (5-10 μA) are insufficient to nucleate bubbles on a 0.38-mm-diameter platinum wire. The hydrolysis gases simply dissolve into solution. However, millimeter-scale EK pumps can draw currents of 3 mA which generate visible bubble growth in a few seconds. The result is that the current fluctuates and decreases to trivial currents if a bubble blocks the fluid path. Hence, gas-bubble-free electrodes have been developed for stable long-term operation.

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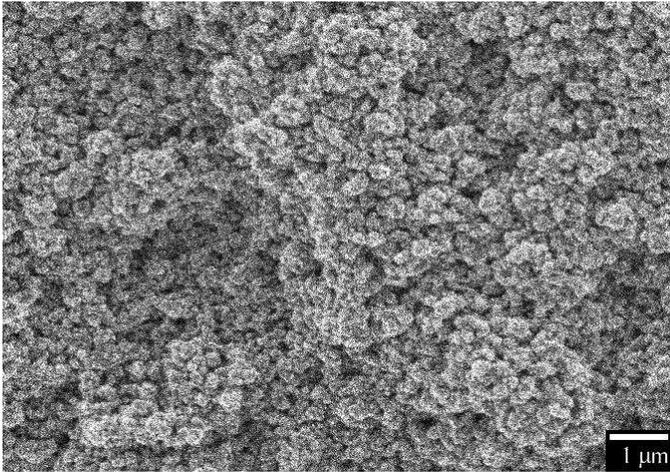


Figure 1. FRACTURE SURFACE OF A POROUS METHACRYLATE POLYMER MONOLITH THAT HAS BEEN DRIED BY SUPERCRITICAL CO₂ EXTRACTION.

1 POLYMER MONOLITH

Porous polymers offer the advantages of rapid fabrication, tunable pore size distribution, and a broad useful pH range (2–12). Monoliths may be microns to meters in size provided at least one dimension is less than a few centimeters to provide for uniform and consistent curing. Fabrication of porous polymers for mobile monolith valves and capillary and chip-based electrochromatography has been described previously [4, 9–12]. Typically, solvents, monomers, and initiator are combined and cured thermally or with ultraviolet light. The pore size distribution is strongly affected by the relative concentrations of the mixture components.

Our solvent mixture was composed of the following spectroscopy-grade chemicals from Aldrich: 1.74 mL of acetonitrile, 535 μL of ethanol, and 400 μL of 5 mM phosphate buffer at pH 6.8. The methacrylate monomer mixture was composed of: 330 μL ethylene glycol dimethacrylate, 435 μL butyl methacrylate, 530 μL tetrahydrofurfuryl methacrylate, and 5 μL methacryloyloxyethyl trimethylammonium methyl sulfate (80% in water). All monomers were purified to remove methyl hydroquinone inhibitors by solid-phase extraction through aluminum oxide and silica sand. The monomers and solvents are mixed with 5 mg of Irgacure 1800 (Ciba, NY) ultraviolet initiator, degassed, and pipetted into 8-cm-long segments of translucent FEP tubing (3.18-mm I.D., 6.35-mm O.D., Berghof) capped with rubber septa (Suba-seal, Aldrich). The apparatus is placed inside an ultraviolet light oven (Spectrolinker XL-1500) for 30 minutes. The monolith is pushed out of the tubing and stored overnight in methanol to dilute the residual uncured solvent mixture.

Drying the monoliths in air is sufficient to crack them into millimeter-size pieces. To avoid cracking, the monolith is ex-

tracted with supercritical CO₂ (ISCO Supercritical Fluid Extractor SFX 220). The diameter decreases from 3.4 mm to 2.7 mm. A SEM image of the extracted polymer is shown in Fig. 1. Epoxy (ScotchWeld DP-420 black, 3M) bonding is accomplished by encapsulating the monolith inside a threaded (1/4-28) polyetheretherketone (PEEK) tube with a 3.2-mm I.D. that has been internally threaded (6-32). The epoxy is dried overnight and then cured at 49°C for an hour. The threaded PEEK tube is ground at both ends until clear cross-sections appear.

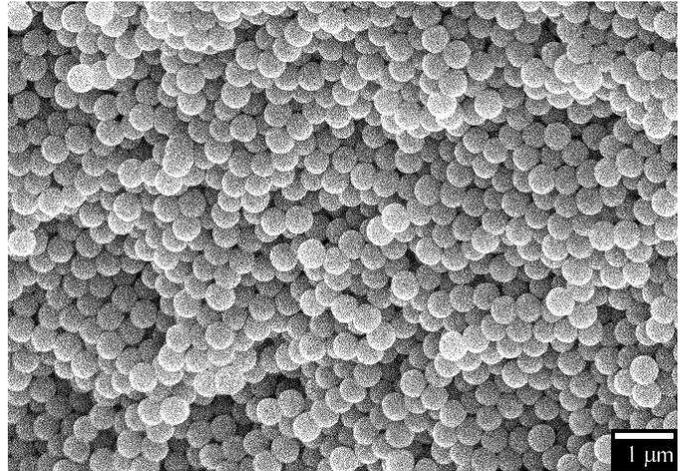


Figure 2. INTERIOR FRACTURE SURFACE OF A SINTERED SILICA MONOLITH COMPOSED INITIALLY OF SLURRY PACKED 0.5- μm PARTICLES. SOME NECKING, SEVERAL VACANCIES, AND LOCALLY ORDERED REGIONS ARE VISIBLE.

2 SILICA MONOLITH

Sintering silica green forms has been demonstrated by others for the purpose of fabricating sub-micron grain size ceramics [5, 6, 13]. Sintered silica monoliths have also been used recently as synthetic opals for optical switches [14–17]. Sacks and Tseng [5] achieved relative densities greater than 99.5% by sintering a green form created by sedimentation of 0.5- μm silica beads. It was observed that sintering causes the entire pore size distribution to shift to smaller pores. Beads were fabricated by the Stöber process [18].

Slurry packing at high pressure against a stainless steel frit was performed with dilute (1% by mass) solutions of monodisperse silica spheres (0.5- μm diameter) suspended in dilute ammonium hydroxide (pH 10). The packing was then dried for 90 minutes at 90°C. Sintering was accomplished with the following thermal profile: 5°C/min rise to 1050°C, hold for 90 minutes,



Figure 3. A SINTERED SILICA MONOLITH WITH A DIAMETER OF 2.8 mm (LEFT) AND AN EPOXY-BONDED MONOLITH (RIGHT).

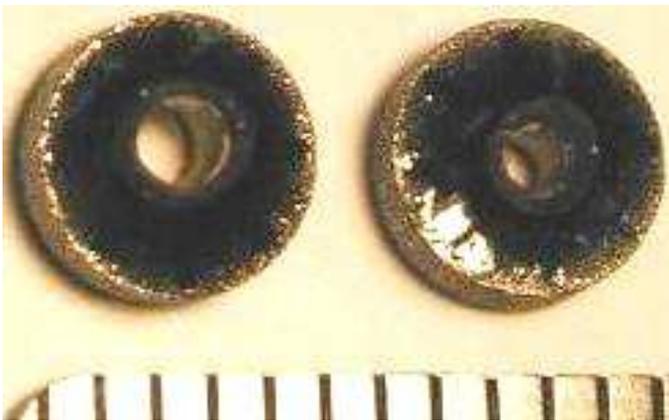


Figure 4. GAS-BUBBLE-FREE CATHODES WITH IONOMER TUBING BONDED INSIDE EPOXY-COATED TITANIUM FRITS. THE SCALE UNITS ARE mm.

and cool at 10°C/min. A monolith forms with a 2.8-mm diameter as shown in Fig. 3, which is 10% less than the tube I.D.. Epoxy bonding and machining is similar to the polymer process.

3 GAS-BUBBLE-FREE ELECTRODES

Gas-bubble-free electrodes have been developed that permit water hydrolysis but isolate the gases from the electrolyte.

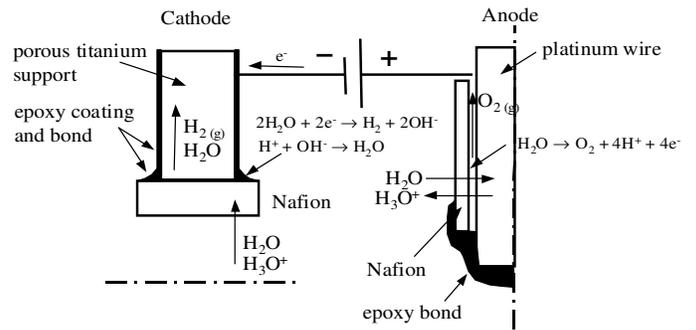


Figure 5. SCHEMATIC OF GAS-BUBBLE-FREE ELECTRODES (NOT TO SCALE) SHOWING THE RELEVANT ELECTROCHEMISTRY AND TRANSPORT. WATER IS OXIDIZED AT THE ANODE TO FORM PROTONS AND OXYGEN. WATER IS REDUCED AT THE CATHODE TO FORM HYDROGEN AND HYDROXYLS. PROTONS ARE REDUCED AT THE CATHODE TO FORM WATER. WATER IS TRANSPORTED TO THE CATHODE BY ELECTROPHORESIS OF HYDRATED PROTONS AND TO THE ANODE BY DIFFUSION ACROSS THE THIN (25-40 μm) MEMBRANE.

Two high-current, compact electrodes have been developed with Nafion[®] (DuPont[™]) tubing from PermaPure: a high-pressure flow-through cathode and a flexible anode. Nafion[®] is a cation-conductive polymer (i.e. a charge-selective salt bridge) that permits diffusive and electrophoretic transport of cations and water.

The high-pressure cathode is shown in Fig. 4. It consists of Nafion[®] tubing (1.3-mm I.D., 1.5-mm O.D.) bonded inside a titanium frit with faces that have been sealed with epoxy. A titanium frit with 2-μm porosity is used as a cathode metal because it provides an exit path for electrolysis gases and a rigid mechanical support for squeezing an o-ring to achieve a high-pressure seal. Titanium is chemically stable as a cathode in EK pump electrolytes.

The left side of Fig. 8 shows the flexible anode bonded inside a modified syringe barrel. It consists of a small diameter (130-μm O.D.) platinum wire inside a small diameter (200-μm I.D., 280-μm O.D.) Nafion[®] tube. The tubing is epoxy bonded to the wire at one end. The other end is threaded through and sealed in a via hole through the housing (here, a syringe barrel). The wire is then soldered to a structural terminal. Figure 8 shows both electrodes in an EK pump assembly.

The Nafion[®] tube has a thin wall (25-40 μm) that results in rapid water diffusion to the platinum, despite the opposing electrophoretic transport of hydrated protons. Platinum is the preferred anode metal because it does not passivate (oxidize) while receiving electrons and is chemically inert in strong acids and bases. Testing has shown that this anode configuration can supply more than 2 mA/cm (23 mA/cm² and 31 mA/cm² based on the tube O.D. and I.D., respectively) in 5-

mM Tris(hydroxymethyl)aminomethane-hydrochloride (TRIS-HCl) at pH 8.5. Operating as a cathode, slugs of water can be seen moving through the coil towards the exit. However, during high-current testing (2 mA/cm) a small number of bubbles appeared during startup and shutdown. Bubbles did not appear to be evolving during constant current operation over a period of minutes. Bubbles have not been observed on the tubing during EK pump operation.

Figure 5 is a schematic of the relevant electrochemistry and transport associated steady-state operation of the gas-bubble-free electrodes with pure water. Electron transfer occurs at the metal-Nafion[®] interface and involves water and proton reduction at the cathode and water oxidation at the anode. In steady-state, water is transported to the cathode by diffusion and electrophoretic transport of hydrated protons. Water is transported to the platinum anode by diffusion alone, which requires a large surface area and/or a thin membrane. For common EK pump electrolytes such as 5-mM TRIS-HCl at pH 8.5, the schematic in Fig. 5 does not change substantially. The reactants and products are the same because the concentration of TRIS⁺ is negligible relative to water (1.3 mM TRIS⁺ vs. 55 M water), and electrophoretic transport of TRIS⁺ through Nafion[®] is slower than proton transport. A pH gradient from high pH at the cathode to low pH at the anode will develop because electrophoresis of TRIS⁺ and Cl⁻ will carry most of the current due to their large concentration relative to protons and hydroxyls. A reduction in pH adversely affects silica EK pumps by reducing the magnitude of the zeta potential (fewer charge sites per area) and, hence, their efficiency. In practice, this problem is avoided by flowing sufficient buffer to avoid pH changes. Alternately, some of the high pH fluid exiting the pump may be returned to the entrance reservoir.

4 EK PUMP PERFORMANCE

The EK actuator is unique in its hydraulic power and pressure capability for its size and its ability to operate without generating gas bubbles. Polymer performance of 3 psi/V (21 kPa/V) and 1% efficiency is a factor of 15 better than published millimeter-scale EK pump performance [19]. Silica monolith performance of 9 psi/V (55 kPa/V) and 3% efficiency is comparable to demonstrated capillary performance [8]. To the best of our knowledge, the porous polymer and silica monoliths have the highest efficiency of any millimeter-scale or larger EK pump to date. The gas-bubble-free Nafion[®] electrodes described above are unique in their ease of fabrication and use; general applicability to aqueous systems, particularly electrolytes with low conductivity; chemical inertness; high-pressure capability (for the cathode); and compact dimensions. Electron transfer with water as the reactant permits larger currents than are possible with methods such as minimizing hydrolysis by adding electrolyte additives with low reduction potentials (e.g. ferro-ferricyanide, nitrate/nitrite, iodide/iodine). This is particularly advantageous for

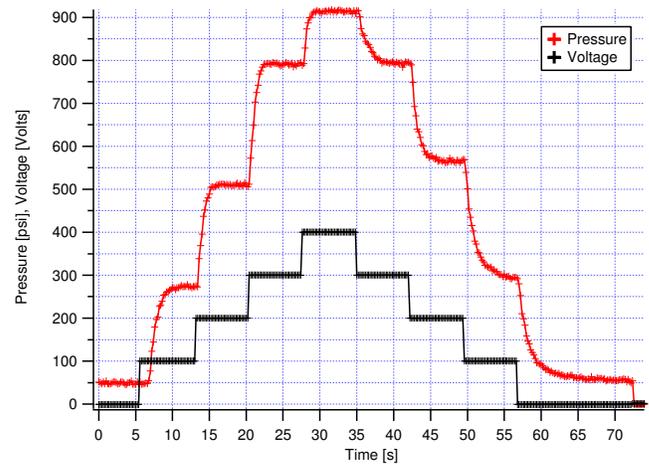


Figure 6. TRANSIENT PRESSURE RESPONSE OF A SILICA EK PUMP WITH A CLOSED EXIT. THE FLUID IS 5-mM TRIS WITH 1.25-mM HEPES AT pH 8. THE TRANSIENTS ARE THE RESULT OF SYSTEM COMPRESSIBILITY.

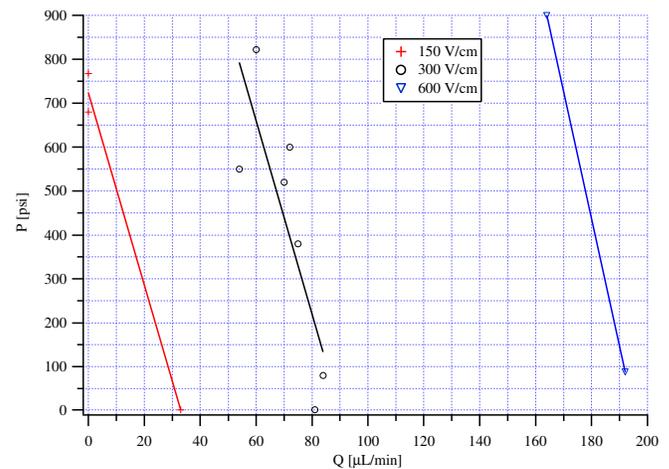


Figure 7. SILICA EK PUMP PERFORMANCE AT ELECTRIC FIELD STRENGTHS OF 150, 300, AND 600 V/cm. THE Y-INTERCEPTS, I.E. THE MAXIMUM PRESSURE POINTS, INCREASE NONLINEARLY DUE TO HEATING.

EK pumps because additives increase the conductivity and decrease the EK pump efficiency.

Figure 6 shows the transient pressure response to step changes in electric field for a silica EK pump with a closed exit. The pump fluid is 5-mM TRIS with 1.25-mM 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) at pH 8. The apparent psi/Volt is 2.5 for the first three voltage steps and decreases to 2.3 for higher field strengths because there is a

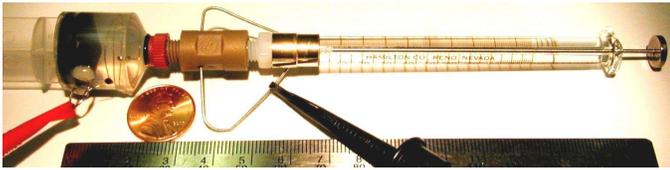


Figure 8. EK PUMP WITH GAS-BUBBLE-FREE ELECTRODES AND A 100- μL SYRINGE ACTUATOR. THE GAS-BUBBLE-FREE ANODE INSIDE THE SYRINGE BARREL IS COMPOSED OF A 10-cm-LONG COIL OF A 130- μm O.D. PLATINUM WIRE INSIDE A 200- μm I.D./ 280- μm O.D. NAFION[®] TUBE SEALED WITH EPOXY ON THE INTERNAL END AND OPEN TO ATMOSPHERE EXTERNAL TO THE RESERVOIR.

small leak at high pressure. The transients for each voltage step take 5 to 7 seconds to reach steady-state due to system compressibility.

Figure 7 shows EK pump performance data for a pump capable of 8 psi/Volt (55 kPa/V). The partial load conditions were observed using masses on a syringe plunger to maintain constant pressure during 15 to 60 seconds of piston displacement to measure the flowrate. Pressures above 900 psi (6.2 MPa) were not measured due to seal limitations. A pressure of 900 psi (6.2 MPa) at the EK pump face corresponds to 6.3 lbf (28 N) distributed along the monolith. The observed psi/volt decreases slightly above 500 psi (3.4 MPa) due to small leaks, presumably past the o-ring on the outlet side of the EK pump; however, no visible leaks were seen during the experiments. The least-squares fits to the data for constant field strength show a non-linear rise in y-intercept, i.e. higher psi/volt, due to pump heating that lowers the viscosity and allows more current for a given field strength.

5 ACTUATION

High-pressure microhydraulic actuation has been demonstrated with gas-bubble-free electrodes, an EK pump, and syringes with different plunger areas. The actuator shown in Fig. 8 has a 100 μL syringe (1.4-mm plunger diameter). Syringes with a larger plunger area may be used to achieve proportionally larger forces but smaller velocities. Several 1-mm-thick glass microscope slides (25x76 mm) were fractured in 3-point bending with a 3.3-mm-diameter piston driven at 530 psi (3.7 MPa), corresponding to a output force of 6.2 pounds (28 N). The current and voltage were 2 mA at 1500 V. Silica EK pumps have demonstrated flowrates and pressures of 200 $\mu\text{L}/\text{min}$ at 400 psi (2.8 MPa) and 100 $\mu\text{L}/\text{min}$ at 1000 psi (6.9 MPa) for driving loads of 2.1 and 5.3 pounds (9.3 and 24 N) at velocities of 1 and 0.5 mm/s, respectively, with a 2.2-mm diameter piston. Long-stroke actuation has been demonstrated by lifting 2 pounds (9 N) at 1 mm/s over 7 cm using a 100- μL syringe. Hydraulic power up to 17 mW has been demonstrated by an 8-psi/Volt (6.9 kPa/V) pump delivering 164 $\mu\text{L}/\text{min}$ at 900 psi (6.2 MPa). These pow-

ers and forces compare favorably with electromechanical actuators of comparable size (solenoid, piezoelectric, stepper motor). The pump and electrodes contain no moving parts and operate silently, which is beneficial for applications requiring actuation with low noise and vibration levels.

6 CONCLUSIONS

High-pressure microhydraulic actuation driven by millimeter-scale electrokinetic pumps with gas-bubble-free electrodes has been demonstrated. High-performance porous polymer and sintered silica monoliths have been developed that give 1% and 3% electric-to-hydraulic work conversion efficiencies, respectively. Flowrates up to 200 $\mu\text{L}/\text{min}$, pressures up to 1200 psi (8.3 MPa), and hydraulic powers up to 17 mW have been observed. Electrokinetic pressures of 3 psi/Volt (21 kPa/V) and 8 psi/Volt (6.9 kPa/V) have been demonstrated. Gas-bubble-free electrodes have been developed that permit extended hermetic operation. EK actuators are capable of forces and powers comparable to electromechanical actuators of similar size.

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