



Creep behavior of the solid acid fuel cell material CsHSO₄



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ABSTRACT

Solid acid materials have recently shown great promise as solid-state electrolytes in intermediate temperature fuel cells. However, little is currently known about their mechanical properties, some of which could severely limit their application. In this study, the steady state creep behavior of the prototypical solid acid, CsHSO₄, is characterized. In its highly conductive superprotonic state (>141 °C), the material creeps at very high rates, as high as 10^{−2} s^{−1}, at stresses in the application design range of only a few MPa. The steady state creep stress exponent $n \approx 3.6$ and activation energy $Q \approx 1.02 \text{ eV} = 98.8 \text{ kJ/mol}$ are consistent with a dislocation-based creep mechanism.

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Solid acids have received considerable research interest recently due to their potential for application as solid state electrolytes in advanced fuel cell technologies. These materials are formed by stabilizing an oxyanion acid, e.g. H₂SO₄, H₃PO₄, etc., with a cation that provides charge balance without removing all the hydrogen from the original acid, thus producing a solid material that is intermediate between an acid and a salt [1]. Solid acids formed using larger cations, e.g. Cs, Rb, etc., are known to undergo a “superprotonic” phase transition at temperatures in the neighborhood of 200 °C that greatly enhances their proton conductivity to values near 10^{−2} S/cm [1,2]. Of the various superprotonic solid acids, CsHSO₄ has served as an important model material. CsHSO₄ was one of the first solid acids to be experimentally shown to undergo a superprotonic phase transition (at a temperature of 141 °C), and one of the first to be shown as directly applicable in fuel cell technology [3,4]. However, while brittle in its lower temperature phases, CsHSO₄ has been shown to suffer large amounts of plastic deformation at low yield stresses above the superprotonic transition [5]. This suggests that creep could be an issue for these materials when operating under prolonged stresses in a fuel cell environment. Although some attempts have been made to explore the creep behavior of CsHSO₄, no study to date has directly addressed it using well established methods [6]. Thus, the primary purpose of the work described here is to measure and characterize the steady state creep behavior of CsHSO₄.

The CsHSO₄ solid was produced by initially dissolving 210 g of cesium carbonate (99%, Alfa Aesar) in 105 mL of deionized water to which 133.4 g of sulfuric acid (ACS, 95.0%–98.0%, Alfa Aesar) was added dropwise under continuous stirring. The CsHSO₄ precipitated as a fine white powder by adding this solution to 1.2 L of methanol (ACS,

absolute, low acetone, 99.8 +%, Alfa Aesar) and was subsequently separated from the liquid by vacuum filtration. The resulting powder was rinsed with methanol and dried overnight in an oven at 60 °C, after which the drying temperature was raised to 110 °C and the powder further dried for another 4 to 5 days. Each day during the 110 °C drying period, the CsHSO₄ was hand ground with a mortar and pestle to retain a fine powder. The final dried powder was uniaxial pressed at room temperature in a cylindrical compression die for 20 min at a pressure of 125 MPa to produce test specimens for compression testing. The cylindrical specimens were 1.9 cm in diameter with heights ranging from 4.8 cm to 5.0 cm. Using a theoretical density for CsHSO₄ of 3.34 g/mL, the specimen dimensions and weights indicated densities in the range of 95%–99% of theoretical [1,7]. After powder compaction, the specimens were annealed for 24 h at 110 °C.

All uniaxial compression tests were performed at constant engineering strain rate using an MTS 10/GL screw driven testing machine. The test temperature was controlled by mounting the specimen in an environmental chamber in which temperature could be controlled to ± 1 °C by electrical resistance heating. The crosshead velocity was set to achieve a specific constant engineering strain rate, and each specimen was deformed to a total engineering strain of 10%. In each test, the stress was observed to approach a constant upper value, for which a constant strain rate test and a constant stress (creep) test provide equivalent information. Crosshead displacement and load, measured with a 44,482 N load cell, were used to determine engineering stress and strain over the course of a test. Engineering stress and strain were converted to true stress, true strain, and true strain rate through the normal assumptions of volume conservation and uniform deformation along the gauge length. The specimens were compression tested at temperatures of 145 °C, 150 °C, and 160 °C, all of which are above the superprotonic transition (141 °C).

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Fig. 1 shows the true stress–true strain curves for each of the specimens as tested at nominal strain rates 10^{-5} , 10^{-4} , 10^{-3} , and 10^{-2} s $^{-1}$. From the data in the figure, it is clear that the flow stresses needed to drive the imposed nominal strain rates became constant over the course of the test, thus indicating that steady creep conditions were indeed achieved in the constant strain rate tests. The flow stress at 10% total true strain for each test was used as a representative value for the analysis of the steady state creep parameters. Log-log plots of the stress and temperature dependencies of the strain rate are presented in Fig. 2, assuming that steady state creep is described by the simple power law relation:

$$\dot{\epsilon}_{ss} = \alpha \sigma^n e^{-Q/kT} \tag{1}$$

Here, $\dot{\epsilon}_{ss}$ is the steady state creep rate, σ the stress, T is the temperature, n the stress exponent for creep, Q the activation energy, α the creep coefficient, and k is Boltzmann's constant. Fitting the data in Fig. 2 to Eq. 1 indicates that CsHSO $_4$ has a stress exponent n in the range 3.6–3.9 and a creep activation energy $Q \approx 1.02$ eV = 98.8 kJ/mol. A complete listing of the values of α , n and Q is presented in Table 1. Note that the form of the parameter plotted on the vertical axis of

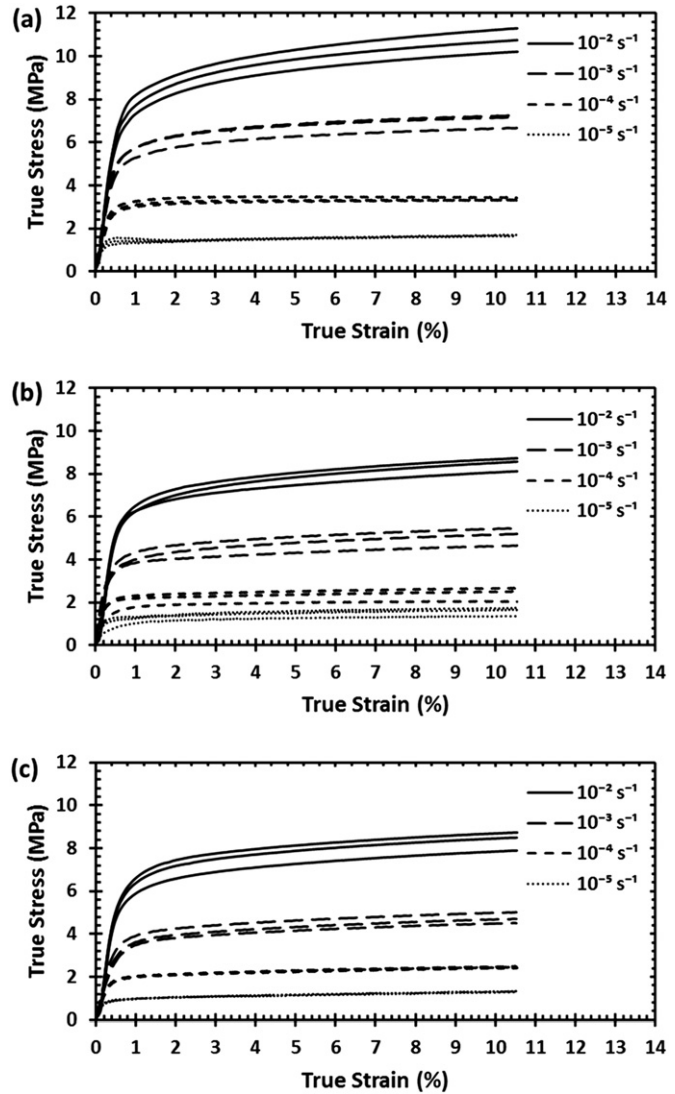


Fig. 1. Stress–strain curves from constant nominal strain rate tests of CsHSO $_4$ specimens tested in compression at three different temperatures: (a) 145 °C; (b) 150 °C; and (c) 160 °C.

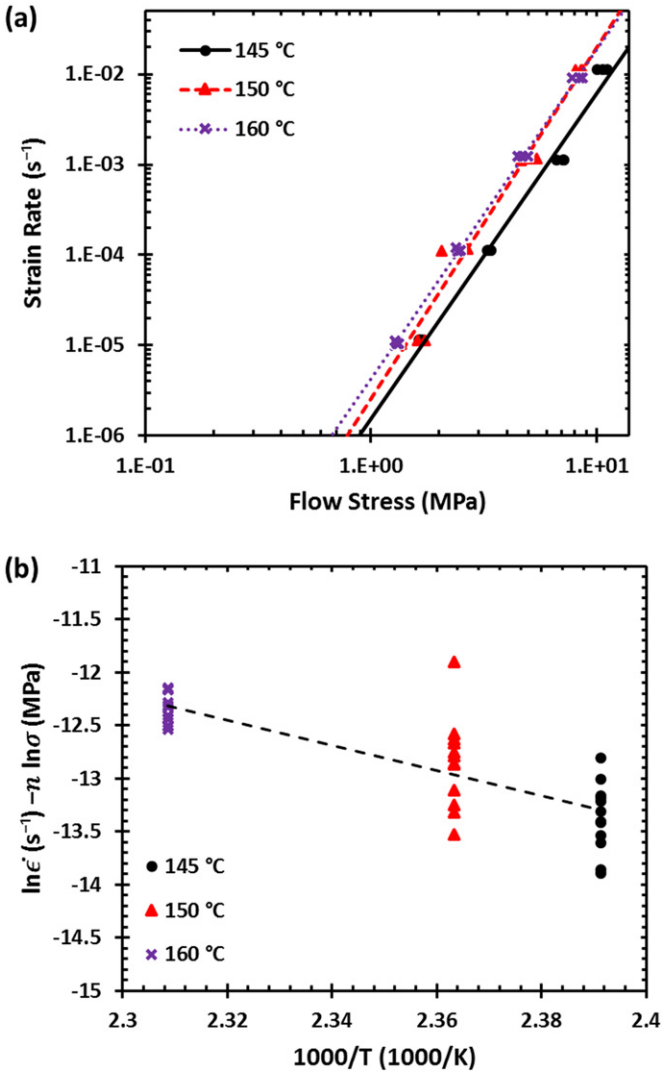


Fig. 2. Steady state creep behavior of CsHSO $_4$: (a) the relation between the steady state flow stress and strain rate for stress exponent determination; and (b) the relation between the stress-compensated steady state strain rate and temperature for activation energy determination.

Fig. 2b is what is needed according to Eq. 1 to extract the activation energy from a plot of the data obtained at all stresses.

Inspection of the experimental data in Fig. 2a reveals that CsHSO $_4$ creeps at a very high rate given the relatively low compressive stresses. This is particularly problematic for traditional fuel cell designs which rely on compressive pressures in the fuel cell stack of the order of a few MPa to seal the device. For stresses of this magnitude, strain rates as high as 10^{-2} s $^{-1}$ are observed in CsHSO $_4$, meaning that any durable CsHSO $_4$ fuel cell design must minimize the load applied directly to the electrolyte.

The measured stress exponent of $n \approx 3.6$ is consistent with a dislocation-based creep mechanism. However, firmly concluding this would require direct microstructural confirmation. Whether or not the

Table 1
CsHSO $_4$ steady state creep parameters determined by fitting the data in Fig. 2 to a function of the form of Eq.1.

Temperature (°C)	n	α (MPa $^{-n}$ s $^{-1}$)	Q (eV)
145	3.59	3.43E + 6	1.02
150	3.87	4.12E + 6	1.02
160	3.63	3.56E + 6	1.02

Table 2

Self-diffusion activation energies for deuterated CsHSO₄ measured at 120 °C, which is well below the superprotonic phase transition of 141 °C [8].

Diffusing species	Self-diffusion energy (eV)
Hydrogen (Deuterium)	0.70 ± 0.03
Cesium	0.60 ± 0.02

measured activation energy of $Q \approx 1.02$ eV supports this assessment is open to interpretation. Although we are unaware of any self-diffusion activation energies for superprotonic CsHSO₄ ($T > 141$ °C), information does exist for deuterated CsHSO₄ just below the transition at 120 °C, as shown in Table 2 [8]. Comparison of the values in the table with the creep activation energy of 1.02 eV shows that while the creep activation energy measured here is larger than the self-diffusion energies for hydrogen and cesium, it is still reasonably close enough to support the possibility of a dislocation controlled creep mechanism rate limited by diffusional processes.

In conclusion, the new experimental data presented in this report suggest that creep may be an important issue in fuel cell designs based on CsHSO₄ electrolytes. In the useful superprotonic temperature range, the material creeps at very high rates with a stress exponent $n \approx 3.6$ and creep activation energy $Q \approx 1.02$ eV = 98.8 kJ/mol.

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