(**Support information**)

Intensively Enhanced Conductivity of Polyelectrolytes by Amphiphilic Compound Doping

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Methanol permeability and selectivity

Methanol permeability is another transport property which is crucial to direct methanol fuel cells. Methanol crossover can lead to significant performance losses, impacting the cathode kinetics, and overall fuel efficiency. As shown in Table S1, Nafion-117 is known to be highly methanol permeability; its methanol permeability is measured as 2.2×10^{-6} cm^2 s^{-1}. In general, the methanol permeability of s-SISH*x* membranes increases as the PSA weight ratio and the corresponding water content raises. It is owing to that the methanol permeates through the membranes in the complex forms such as $CH_3OH_2^+$ and H_3O^+. Thus, it could be concluded that membranes with higher PSA ratio increase the water engaged with sulfonic acid groups and gradually increased methanol permeability. In order to understand the performance trade-off between permeability and conductivity, we used the selectivity representing the transport characteristics of both the proton and methanol (σ/P) of the hybrid membranes and Nafion-117, as shown in Figure S1. Membrane s-SISH2.0 is most selective than other s-SISH*x* membranes.

Table S1. The methanol permeabilities of the s-SISH*x* membranes .

Ionomer	MeOH permeability (cm^2 s^{-1})
Nafion-117	2.2×10^{-6}
s-SISH	1.1×10^{-6}
s-SISH0.5	3.2×10^{-6}
s-SISH1.0	4.8×10^{-6}
s-SISH1.5	5.2×10^{-6}
s-SISH2.0	5.4×10^{-6}
s-SISH2.5	5.8×10^{-6}
s-SISH3.0	6.2×10^{-6}

[a] The proton conductivity at 95 % R.H.

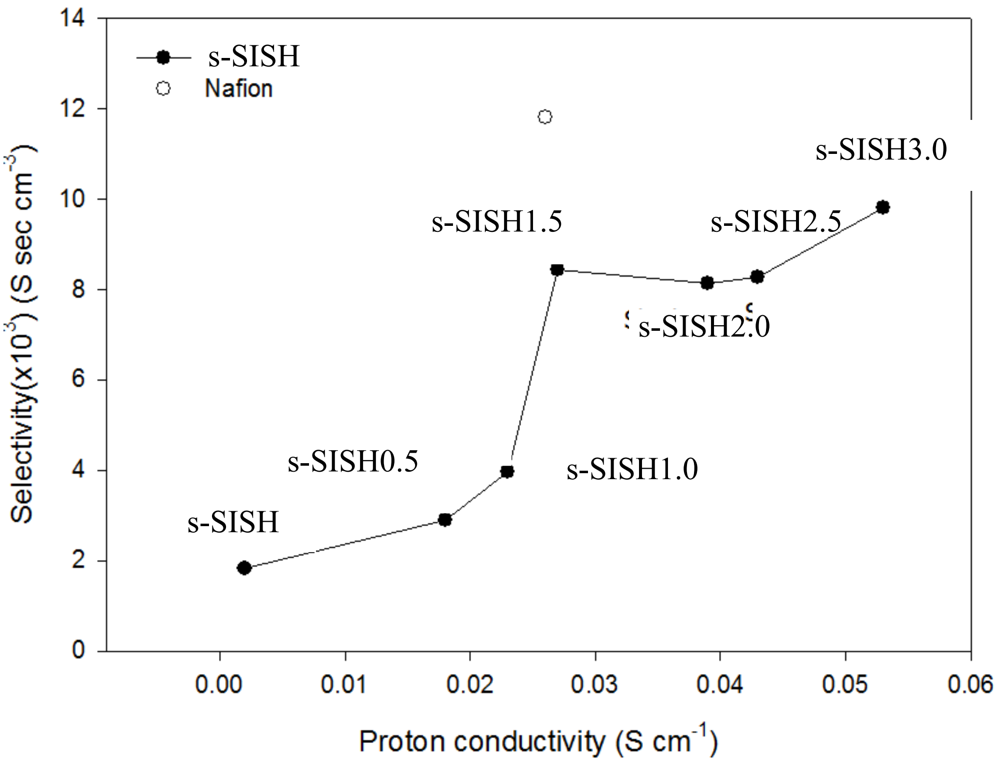

Figure S1: The performance trade-off plot of conductivity versus selectivity of hybrid membranes and Nafion-117.

Single DMFC Performance

The performance of the membrane electrode assemblies (MEAs) in the DMFC with membrane s-SISH, s-SISH20 and Nafion-117 as electrolyte membranes, E-TEK 20% Pt/XC-72 as cathode, and E-TEK 20% Pt-Ru/XC-72 as anode, was evaluated in a single DMFC. The electrolyte membrane was sandwiched between the cathode and the anode by hot pressing. The s-SISH2.0 membrane exhibits a higher current density than s-SISH by 8.9 $mAcm^{-2}$ in the ohmic resistance region (0.199 V), as shown in the polarization curves of Figure S2. The corresponding power density curves of these MEAs are also displayed in Figure S2. Membrane s-SISH2.0 (4 $mWcm^{-2}$) shows a better power density, which is 2.28 times higher than that of s-SISH (1.75 $mWcm^{-2}$).

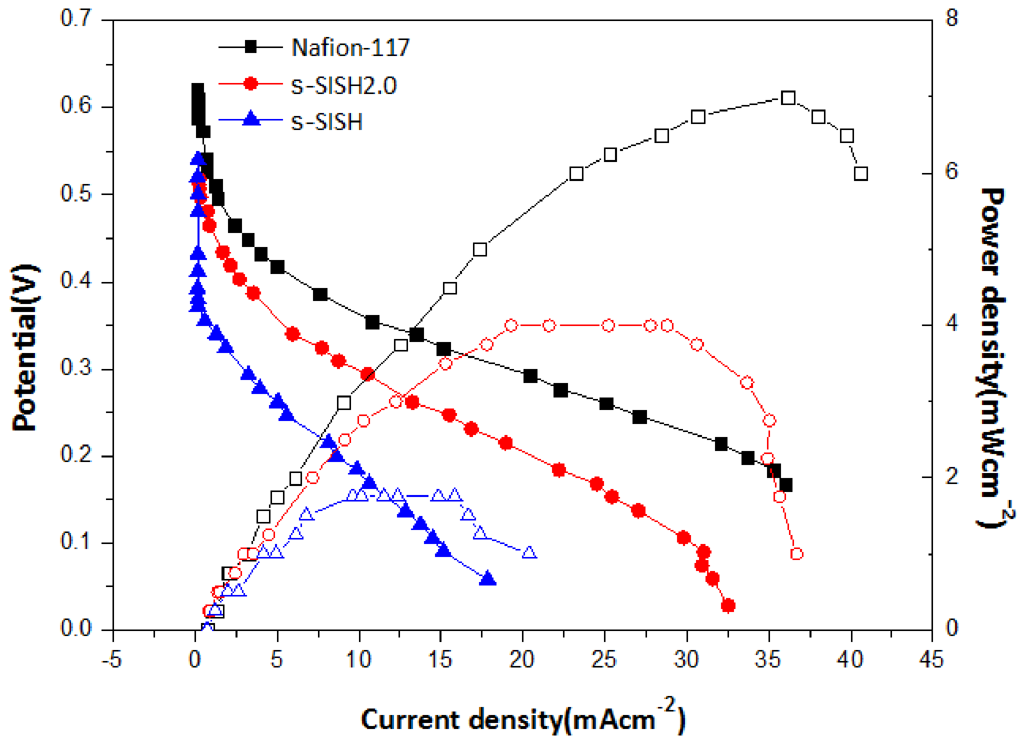

Figure S2: Comparison of polarization curves for the single DMFC with Nfion-117, s-SISH and s-SISH2.0 as the electrolyte membrane (cell temperature: 60 ^{o}C; anode: 2 ml/min of 2.0M methanol; cathode: O_2; flow rate: 100 ml min^{-1}; atmospheric pressure).