

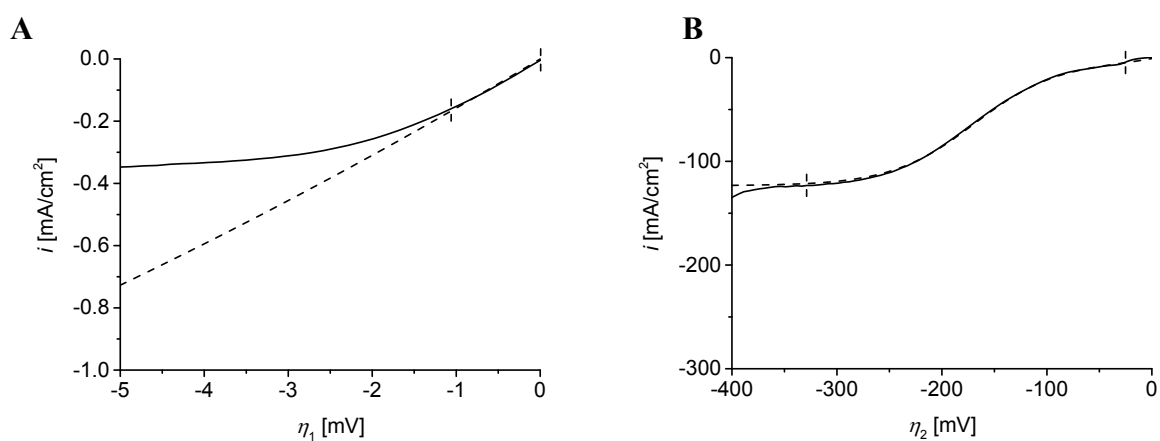
## Chain Length Variation to Probe Mechanism of Accelerator Additives in Copper Electrodeposition

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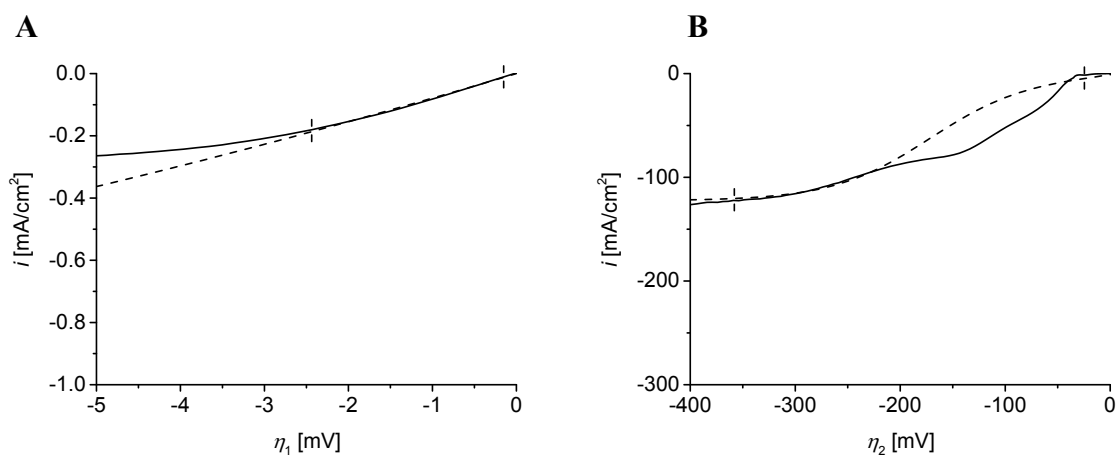
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### Supporting Information



**Figure S1.** (A) Experimental LSV data for VMS with chloride and SES (solid line) and corresponding fit with equation (3) (dashed line). (B) Experimental LSV data for VMS with chloride and SES (solid line) and corresponding fit with equation (2) (dashed line).



**Figure S2.** (A) Experimental LSV data for VMS with chloride and SBS (solid line) and corresponding fit with equation (3) (dashed line). (B) Experimental LSV data for VMS with chloride and SBS (solid line) and corresponding fit with equation (2) (dashed line).

In accordance with [T. P. Moffat, D. Wheeler, D. Josell, *Journal of The Electrochemical Society* **2004**, *151*, C262-C271.], no attempt was made to describe the peak(s) evident at overpotentials between approximately -50 mV and -200 mV.

**Table S3.** Raman mode assignments.  $\nu$  = stretch,  $\delta$  = bend,  $\tau$  = torsion,  $\rho$  = rock,  $\omega$  = wag

<u>Peak</u>	<u>Observed Raman Shift (cm<sup>-1</sup>)</u>						<u>Assignment</u>	<u>References</u>
	SES	SPS	SBS	SES + Cl <sup>-</sup>	SPS + Cl <sup>-</sup>	SBS + Cl <sup>-</sup>		
<b>a</b>	290	289	294				$\nu(\text{Cu-SO}_4)$	1-6
<b>b</b>				287	280	277	$\nu(\text{Cu-Cl})$	2-4,7-9
<b>c</b>				371			undefined $\tau$ -mode	10
<b>d</b>	435	441		439	441		$\delta(\text{CCC/CCS})$	11-13
<b>e</b>	527	529	530	528	531	535	$\rho(\text{SO}_2)$	10,14
<b>f</b>	570	569		571	566		$\delta(\text{SO}_2)$	10
<b>g</b>	616	617	609	612	620	609	<i>gauche</i> $\nu(\text{C-S})_{\text{thiol}}$	12,15-18
<b>h</b>	632			631			<i>gauche</i> $\nu(\text{C-S})_{\text{thiol}}$	9,12-19
<b>i</b>	683	677	680	693	681	679	<i>trans</i> $\nu(\text{C-S})_{\text{thiol}}$	9,12,13,16,18,19
<b>j</b>	725	733	726		733	726	$\rho(\text{CH}_2)$	9,13-15,17
<b>k</b>	787	794	790	794	796	791	$\nu(\text{C-SO}_3)$	9,19,20
<b>l</b>		849			851		$\rho(\text{CH}_2)$	9,12
<b>m</b>	907	916		900	917		$\rho(\text{CH}_2)$	11,13
<b>n</b>		957			952		<i>gauche</i> $\nu(\text{C-C})$	12
<b>o</b>	970	968	972			969	$\nu(\text{SO}_4^{2-})$	3,5,6,8,9,15
<b>p</b>	1023	1024	1026	1034	1033	1026	<i>trans</i> $\nu(\text{C-C})$	13,18
<b>q</b>	1210	1206	1200				$\nu(\text{SO}_2)$	6,9,14,20-22
<b>r</b>	1240	1231	1248		1240	1248	$\omega(\text{CH}_2)$	9,11,14,17,20
<b>s</b>	1288	1271	1304	1294	1271	1303	$\omega(\text{CH}_2)$	9-12,23,24
<b>t</b>		1345	1353		1345	1347	$\delta(\text{CH}_2)$	9,11,24
<b>u</b>	1404	1417	1418	1407	1416	1413	$\delta(\text{CH}_2)$	9,11,14,23

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