Communication

Thermal Properties of Söderberg Electrode Materials

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Thermal properties of green Söderberg electrode pastes were measured up to 1073 K (800 °C) using the transient plane source method. Comparison was made to measurements on an electrode material baked beforehand to 1473 K (1200 °C). For the green pastes, thermal conductivity was found to decrease up to 673 K (400 °C) at the onset of baking. After about 873 K (600 °C), thermal conductivity of the material increases with increasing temperature. For previously baked Söderberg material, thermal conductivity continually increases with increasing temperature.

Söderberg electrodes have been employed for the past 100 years in submerged-arc electric furnaces in ferroalloy smelting, platinum, nickel and copper matte smelting, and slag cleaning. Nowadays, Söderberg electrodes of 2 m in diameter are commonplace. The primary operational advantage of the Söderberg electrode is that it is self-baking and operation is continuous. As the electrode is consumed within the furnace and slipped downwards, fresh green electrode paste in the form of blocks, cylinders or briquettes is intermittently charged from the top into a supporting steel electrode casing.

Traditional Söderberg electrode paste is a composite material comprised of 70 to 80 pct granular carbon aggregate (calcined anthracite or petroleum coke and graphite) and a coal tar pitch binder.[1] The material softens as it heats up and flows to fill the electrode casing. As the electrode column is gradually slipped downwards and is heated by electrical resistance from the electrode current as well as heat emanating from the furnace, carbonization of the binder continues until the soft paste transforms into a solid material, or is baked,

being finished between 673 K and 773 K (400 °C to 500 °C).[2-4] An excessive slipping rate can push the baking zone below the contact clamps and potentially lead to catastrophic soft breakage of the electrode.

During furnace operation high temperatures, electrical currents, and electrode movements make it very difficult to continuously monitor electrode operation *in situ* by direct measurement, although some have measured temperature profiles in limited measurement campaigns.[2] As such, finite-element thermal and thermoelectrical models of electrodes have been developed and used in industry for several decades to estimate isotherms within an electrode to optimize operation. Previous work has been published regarding modeling and simulation of thermal profiles in Söderberg electrodes, though primarily in conference proceedings.[2,4,5]

However, the reliability of an electrode model is inherently limited by the accuracy of temperature-dependent electrode material property data. Particularly important to be determined by a model is the position of the baking isotherm in the electrode column. Söderberg electrode paste is rather complex, and drastic physical and compositional changes occur in the material during the baking process. The present work focused on measurement of thermal conductivity of electrode material during heating from room temperature through the process of baking, and up to 1073 K (800 °C).

For thermal conductivity measurements, the method deemed most suitable for this material in the temperature range of interest is the Transient Plane Source (TPS) method. This method is particularly suitable for investigation of the thermal conductivity but may also be used for measuring the thermal diffusivity and heat capacity. The method was originally developed in Sweden at Chalmers University of Technology. Today the method is commercialized by the company Hot Disk AB. The TPS method is specifically developed for metals, ceramics, polymers and other common solid materials, but it can also be used for liquids. It is possible to measure thin insulating films (ranging from 10 to 600 microns), sheets with high thermal conductivity or anisotropic thermal properties of bulk materials.

The TPS method utilizes a flat sensor comprised of a double spiral etched out of very thin nickel foil laminated between two layers of electrically insulating film (polyimide Kapton or mica). The sensor is clamped between two halves of the sample material to be measured, as illustrated in Figure 1(a). The sensor acts as both the heat source and as a resistance thermometer. The sensor is heated by a pulse of constant electrical current for a given time. The current heats the sensor and thus a change in its resistance will occur. The resulting temperature increase depends on the current (power) supplied and the heat conducted away through the surrounding sample material. The voltage of the sensor is measured and since the current is held nearly constant by a resistance bridge, the voltage change is

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proportional to the change in the resistance of the sensor. The voltage is recorded by a digital voltmeter to determine the temperature increase of the sensor. Based on the temperature increase, the system evaluates the thermal properties of the material.[6] Details of thermal conductivity measurements and corresponding calculations with this technique can be found in the work of Gustafsson.[7]

In order to avoid boundary effects, the thickness of the sample is not to be less than the radius of the hot disk sensor.[6] The commercial electrode paste samples were prepared by cutting them with a diamond saw in pieces of 15 mm radius and 26 mm thickness and then polished with emery paper and water. Finally, they were dried for 24 hours before performing measurements. The sensor was then sandwiched between upper and lower sample halves. Three different materials were studied: two green Söderberg pastes with 338 K (65 °C) and 363 K (90 °C) softening points, and for reference, Söderberg 90 °C s.p. paste material that was baked beforehand to 1473 K (1200 °C). Table I lists the sample materials and experimental conditions.

After sample preparation, the thermal conductivities of all samples were measured at room temperature.

Several repeat measurements were performed at each temperature. The measuring equipment was a Model TPS3500 located at Swerim AB.

A Kapton sensor with a 6.4 mm radius (Hot Disk 5501) was used in the experiments up to 473 K (200 °C). The sample/sensor was contained in a chamber furnace in ambient atmosphere. Since most of the measurements were conducted above the softening point of the binder and below the baking isotherm, the sample was contained in an alumina crucible with 50 mm inner diameter and 60 mm depth. The electrical pulse power was set at 400 mW for the Kapton sensor.

For the measurements above 473 K (200 °C), a mica-insulated sensor was employed (Hot Disk 5082, 6.6 mm radius, maximum temperature of 1073 K (800 °C). The sensor/sample assembly was placed inside a horizontal resistance furnace within a ceramic tube 1.5 m in length and 6 cm in diameter that was sealed on both ends with water-cooled caps. Insulation was placed in the ends of the tube. Argon gas with very low flow rate was passed through the furnace tube to prevent oxidation of the paste samples and degradation of the sensor at high temperature. To prevent the effect of the furnace convection on the measured sample, the sample was
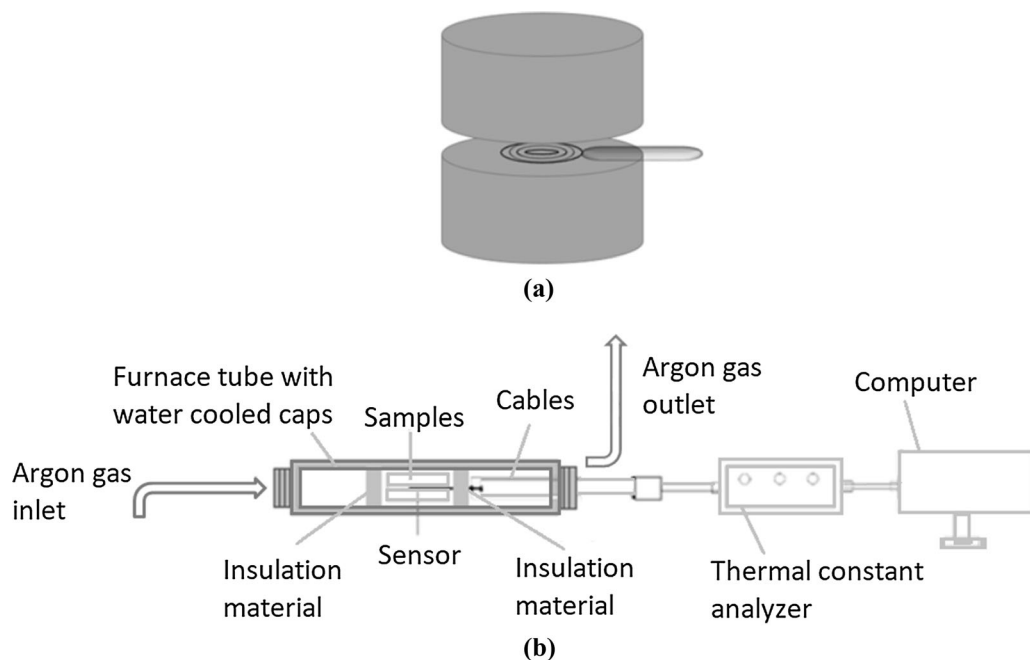

Fig. 1—(a) Hot Disk sensor and sample; (b) schematic of the experimental furnace setup for the measurements above 473 K (200 °C).

Table I. Electrode Materials and Experimental Conditions

Material	Temperature Range [K (°C)]		Sensor Insulation	Heating Power [mW]	Recording Time [s]
Electrode paste 65 °C softening point	295 to 473	(22 to 200)	Kapton	400	10
	473 to 1073	(200 to 800)	Mica	800	10
Electrode paste 90 °C softening point	295 to 473	(22 to 200)	Kapton	400	10
	473 to 1073	(200 to 800)	Mica	800	10
Electrode paste baked to 1200 °C	295 to 473	(22 to 200)	Kapton	400	20
	473 to 1073	(200 to 800)	Mica	800	20

placed in the furnace tube covered by insulation material as shown in Figure 1(b). A Type-K thermocouple was used to accurately control the temperature inside the tube, where another Type-K thermocouple was used to control the furnace temperature. A sketch of the experimental setup is shown in Figure 1(b).

Repeat measurements were taken with a relaxation time (time between repeated measurements) of 10 minutes. Every time the furnace achieved the next level in target temperature there was a rest time of 100 minutes so that the conditions in the chamber were stabilized and the samples were at the correct temperature. In such a way, temperature drift did not occur during the measurements, and so there was no need for temperature drift compensation prior to calculating the thermal properties of the materials. The electrical pulse power was set at 800 mW for the mica sensor.

The total time of the measurement is short enough such that the outer boundaries of the sample do not influence the temperature increase, i.e. the sensor can be considered in contact with an infinite or semi-infinite solid.[7] The time of electrical pulse should be approximately r^2/κ, where r is the sensor radius and κ is the thermal diffusivity.[6] The corresponding times were 20 seconds for the baked electrode material and 10 seconds for the pastes.

Measured thermal property values for all three materials with increasing temperature are given in Tables II, III, and IV. All the materials were tested from room temperature up to 1073 K (800 °C). The tabulated values at each temperature are the mean values after repeated measurements, with the corresponding calculated standard error values shown in parentheses.

Table II. Measured Values for 65 °C Softening Point Electrode Paste

Temp. [K (°C)]	No. of Meas.	Thermal Conductivity [W m^{-1}K^{-1}]	Thermal Diffusivity [mm^{2}s^{-1}]	Vol. Heat Capacity [MJ m^{-3} K^{-1}]
295 (22)	1	3.26	4.15	0.79
323 (50)	10	2.83	4.41	0.643
		(0.016)	(0.073)	(0.014)
373 (100)	10	2.70	4.27	0.630
		(0.006)	(0.023)	(0.005)
423 (150)	20	2.30	3.68	0.634
		(0.025)	(0.086)	(0.020)
473 (200)	6	1.23	5.34	0.232
		(0.038)	(0.140)	(0.010)
673 (400)	12	0.504	6.49	0.078
		(0.015)	(0.275)	(0.003)
773 (500)	6	0.515	6.71	0.077
		(0.012)	(0.170)	(0.005)
873 (600)	6	0.539	6.85	0.080
		(0.018)	(0.374)	(0.004)
973 (700)	6	1.48	5.32	0.278
		(0.073)	(0.031)	(0.013)
1073 (800)	1	2.57	3.77	0.680

Table III. Measured Values for 90 °C Softening Point Electrode Paste

Temp. [K (°C)]	No. of Meas.	Thermal Conductivity [W m^{-1} K^{-1}]	Thermal Diffusivity [mm^2 s^{-1}]	Vol. Heat Capacity [MJ m^{-3} K^{-1}]
295 (22)	4	2.48	3.58	0.690
		(0.003)	(0.035)	(0.005)
368 (95)	10	2.19	3.20	0.683
		(0.007)	(0.040)	(0.010)
423 (150)	10	2.07	2.85	0.728
		(0.005)	(0.033)	(0.009)
473 (200)	6	1.04	3.73	0.282
		(0.040)	(0.169)	(0.013)
673 (400)	18	0.562	4.33	0.200
		(0.056)	(0.577)	(0.045)
773 (500)	6	0.573	4.39	0.133
		(0.023)	(0.076)	(0.007)
873 (600)	6	0.597	4.83	0.123
		(0.013)	(0.025)	(0.003)
973 (700)	6	1.59	4.59	0.347
		(0.018)	(0.053)	(0.005)
1073 (800)	6	2.75	3.43	0.802
		(0.048)	(0.040)	(0.024)

Table IV. Measured Values for Electrode Paste Pre-baked to 1473 K (1200 °C)

Temp. [K (°C)]	No. of Meas.	Thermal Conductivity [W m^{-1} K^{-1}]	Thermal Diffusivity [mm^2·s^{-1}]	Vol. Heat Capacity [MJ·m^{-3}·K^{-1}]
295 (22)	11	3.86 (0.010)	3.60 (0.097)	1.08 (0.026)
333 (60)	20	3.64 (0.001)	2.31 (0.003)	1.58 (0.002)
373 (100)	20	3.90 (0.002)	2.13 (0.002)	1.83 (0.001)
393 (120)	11	3.94 (0.003)	2.46 (0.004)	1.60 (0.002)
433 (160)	60	4.10 (0.004)	2.34 (0.036)	1.77 (0.015)
473 (200)	60	4.16 (0.014)	2.24 (0.017)	1.86 (0.018)
573 (300)	10	4.44 (0.006)	2.75 (0.040)	1.62 (0.019)
673 (400)	9	5.22 (0.058)	2.40 (0.033)	2.18 (0.010)
773 (500)	10	5.80 (0.073)	2.33 (0.034)	2.49 (0.029)
973 (700)	10	7.30 (0.025)	5.73 (0.034)	1.27 (0.029)
1073 (800)	10	7.97 (0.026)	5.62 (0.117)	1.41 (0.016)
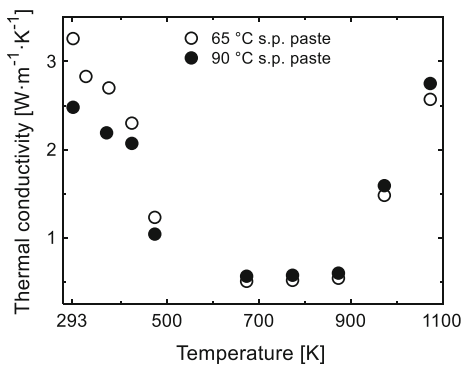
Fig. 2—Thermal conductivity of electrode materials with 65 °C and 90 °C softening point binders.
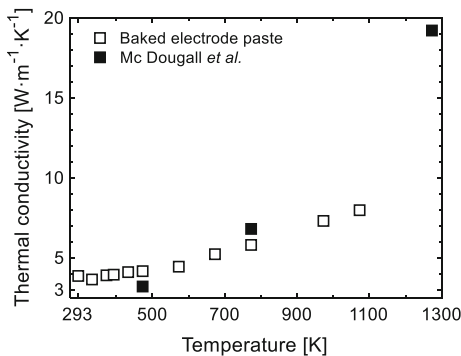

Fig. 3—Thermal conductivity of Söderberg electrode material baked beforehand to 1473 K (1200 °C).

Mean thermal conductivity values as a function of temperature for the three materials tested are presented in Figures 2 and 3.

From Figure 2, it is seen that as the green electrode pastes heat and become fluid that thermal conductivity decreases considerably, bottoming at around 0.5 W·m^{-1}·K^{-1} by 673 K (400 °C). By this temperature, there is no appreciable difference between the paste materials. In the range of 673 K to 873 K (400 °C to 600 °C) thermal conductivity does not change. Above 873 K (600 °C) thermal conductivity steeply increases with temperature, climbing to 2.75 W·m^{-1}·K^{-1} by 1073 K (800 °C) for the latter paste.

Figure 3 shows the increase in thermal conductivity of the pre-baked electrode paste with increasing temperature, which rises nearly linearly from 3.86 W m^{-1}·K^{-1} at 295 K (22 °C) to 7.97 W m^{-1}·K^{-1} by 1073 K (800 °C). For comparison purposes, also included in Figure 3 are tabulated data from Mc Dougall et al.,[4] showing reasonable agreement with the pre-baked electrode material measurements in the present study, though much higher than the values for green pastes seen in Figure 2. This reference provides a good summary of materials properties of electrode paste, and cites Bermudez et al.[5] for the thermal conductivity data (they provide a curve up to 2873 K (2600 °C)), although from that point it is unclear the source of the data.

The thermal conductivities of the green pastes are far below that of the same material baked beforehand across the temperature range studied. The thermal conductivity of the green paste decreases as it becomes fluid and expands with increasing temperature. For both green pastes, above 673 K (400 °C) structural changes

are evident from how the thermal conductivity levels out and increases above 873 K (600 °C). As the paste is heated it transforms as volatile organic compounds are removed and the coal tar pitch binder turns into a solidified carbon substrate. The present work corroborates others well that the baking isotherm for a typical Söderberg electrode paste lies between 673 K and 773 K (400 °C and 500 °C).[1,4] Between the range 673 K to 873 K (400 °C to 600 °C), the thermal conductivity values of the originally green paste materials are an order of magnitude lower than the same paste material baked beforehand. After carbonization, the thermal conductivity of the paste increases nearly linearly with increasing temperature up to 1073 K (800 °C).

With increasing temperature after carbonization, the carbon structure continues to become increasingly ordered as graphite crystallites grow. The thermal conductivity is proportional to crystallite size and so a function of graphitization degree.[8,9] The structural changes in the electrode paste materials are of course irreversible, and consequently the thermal conductivity of electrode paste baked beforehand to 1473 K (1200 °C) is far higher than the green pastes. It is expected that the curves in Figures 2 and 3 would coincide by 1473 K (1200 °C).

In summary, the salient findings of this study are as follows:

- Detailed thermal property data for electrode paste are provided from room temperature up to 1073 K (800 °C), which capture the rapid changes in thermal properties as Söderberg electrode paste melts, heats up and eventually carbonizes.
- The thermal conductivity data of pre-baked electrode material across the temperature range of 673 K to 873 K (400 °C to 600 °C) are an order of magnitude higher than for green paste during the baking process.
- There are no appreciable differences in thermal properties of green pastes with 65 °C and 90 °C softening point binders, which should simplify modeling.

The new data should help to improve accuracy of electrode models in determining the position of the baking isotherm.

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